

# ASSESSING CHANGES IN ELEMENTAL MASS AS A RESULT OF CHEMICAL WEATHERING OF GRANODIORITE IN A MEDITERRANEAN (HOT SUMMER) CLIMATE

GARY H. GIRTY,<sup>1</sup> JEFFREY MARSH,<sup>1</sup> ARON MELTZNER,<sup>1</sup> JESSICA R. McCONNELL,<sup>1</sup> DAMON NYGREN,<sup>1</sup> JOANNA NYGREN,<sup>1</sup> GAIL M. PRINCE,<sup>1</sup> KESLER RANDALL,<sup>1</sup> DIANE JOHNSON,<sup>2</sup> BRETT HEITMAN,<sup>1</sup> AND JENNIFER NIELSEN<sup>1</sup>

<sup>1</sup> Department of Geological Sciences, San Diego State University, San Diego, California 92182, U.S.A.

<sup>2</sup> GeoAnalytical Laboratory, Washington State University, Pullman, Washington 99164-2812, U.S.A.

**ABSTRACT:** In ascending order, relatively unweathered granodiorite, ~ 1.97 m of friable granodiorite, and ~ 0.91 m of very coarse loamy sand make up a well developed weathering profile that developed on a Cretaceous granodiorite lying within a Mediterranean (hot summer) climatic belt in the Peninsular Ranges of southern California, U.S.A. Textural, modal, and chemical data indicate that in the friable granodiorite and in the very coarse loamy sand, plagioclase was leached at a rate faster than was K-feldspar while quartz remained little changed. In addition, molecular Ca and Na were probably leached at a faster rate from plagioclase and titanite than K was leached from K-feldspar and biotite.

Mass-balance calculations show that ~ 3.4% ( $\pm$  2.0%) of the original bulk mass of the friable granodiorite was removed during its development. This loss of bulk mass was accommodated through the removal of ~ 4%, ~ 9%, ~ 18%, ~ 11%, ~ 17%, ~ 29%, and ~ 14% of the masses of Si, Ca, K, Na, P, Ba, and Sr respectively. In addition, the masses of Fe and Y were increased by ~ 12% and 52% respectively. Of the ~ 3.4% loss of original bulk mass, ~ 99% is due to the loss of Si, Ca, K, and Na mass.

The severity of chemical alteration is greatest in samples analyzed from very coarse loamy sand. This conclusion is supported not only by textural relationships, but also by mass balance relationships that show that ~ 11.2% ( $\pm$  2.1%) of the original bulk mass of the very coarse loamy sand was removed during its development. This loss in mass was accommodated through the removal of ~ 12%, ~ 12%, ~ 42%, ~ 14%, ~ 41%, ~ 80%, ~ 21%, ~ 14%, ~ 10%, and ~ 40% of the masses of Si, Mn, Ca, K, Na, P, Ba, Zn, Rb, and Sr, respectively. In contrast, during development of the very coarse loamy sand the masses of Ti and Fe were increased by ~ 17% and ~ 22%, respectively. Of the ~ 11.2% loss of original bulk mass, ~ 99% is attributable to the removal of Si, Ca, K, and Na mass.

Data summarized above, and in work by others, imply that plutonic sediment derived from sources lying within a wide range of climatic conditions, do not reflect directly the bedrock from which they were derived, but instead will mirror the compositions of the weathering profile.

## INTRODUCTION

Chemical weathering is the result of reactions between unstable minerals and the hydrosphere, biosphere, and/or atmosphere (e.g., Johnsson 1993; Nesbitt and Young 1996; Nesbitt and Markovics 1997; Nesbitt et al. 1996; Nesbitt et al. 1997). At the Earth's surface the most important solution involved in chemical weathering is water. Without it natural acids do not form, plants do not grow and thrive, and chemical weathering cannot occur. Chemical weathering proceeds because soil waters form both inorganic and organic acids. These acids in turn react with the mineralogical constituents of bedrock materials such as quartz, plagioclase, and K-feldspar (Nesbitt et al. 1980; Nesbitt and Young 1984, 1989; Johnsson 1993; Nesbitt and Markovics 1997). The three preceding mineralogical phases are typical of granitoids, a common rock exposed at the Earth's surface. However, when in contact with acidic soil solutions quartz, plagioclase, and K-feldspar do not react at the same rate (Nesbitt et al. 1980; Nesbitt and Young 1984,

1989; Nesbitt et al. 1996; Nesbitt et al. 1997; Nesbitt and Markovics 1997). For example, the pH of most soil solutions is between ~ 4 and 5 (Reuss and Johnson 1985; Drever 1988; Nesbitt et al. 1997). The measured leach rate for quartz in dilute solution, under ambient temperature and pressure, and at a pH below 6.0, is between approximately  $10^{-12.5}$  and  $10^{-13.5}$  moles  $m^{-2}s^{-1}$  (Dove and Elston 1992; Nesbitt et al. 1997; Nesbitt and Markovics 1997). In contrast, the leach rates of oligoclase and microcline at pH = 3.0 are  $6.5 \times 10^{-11}$  and  $5.5 \times 10^{-11}$  moles  $m^{-2}s^{-1}$ , respectively (Holdren and Speyer 1985, 1987; Nesbitt et al. 1997; Nesbitt and Markovics 1997). At a pH of 5.0, the leach rates for oligoclase and K-feldspar are  $3.1 \times 10^{-12}$  and  $1.5 \times 10^{-12}$  to  $3.25 \times 10^{-11}$  moles  $m^{-2}s^{-1}$ , respectively (Busenberg and Clemency 1976; Holdren and Speyer 1985; Mast and Drever 1987; Nesbitt et al. 1997; Nesbitt and Markovics 1997). Hence, within most weathering profiles quartz should dissolve less rapidly than do the feldspars (Nesbitt et al. 1997).

Most ground waters contain enough aqueous  $SiO_2$  to be fully saturated with respect to quartz (i.e.,  $> \sim 6$  mg/l for dilute solutions) (Nesbitt et al. 1997; Nesbitt and Markovics 1997). However, natural solutions seldom achieve saturation with respect to plagioclase (Nesbitt et al. 1997; Nesbitt and Markovics 1997), while those with pH  $< 7$  are commonly saturated with regard to K-feldspar (Nesbitt and Young 1984, 1989; Nesbitt et al. 1997). These observations, along with simulation studies of weathering, imply that under steady-state conditions either plagioclase is leached at a rate faster than K-feldspar or that the two feldspars are leached at a constant rate while no appreciable dissolution of quartz occurs under common conditions associated with soil development (Nesbitt et al. 1997). These relationships and their potential effects on modal mineralogy and chemical compositions within weathering profiles are illustrated in Figure 1.

Though pedologists have documented that chemical weathering accommodates the development of soils in arid to Mediterranean climates (e.g., Nettleton et al. 1970; Boettinger and Southard 1991; Jones and Graham 1993; Birkeland 1999; Frazier and Graham 2000), to our knowledge, few if any studies have focused on quantifying changes accompanying chemical degradation of granitoids under such relatively dry conditions. Hence, we undertook a study aimed at quantifying the bulk and elemental chemical changes attending the development of a single weathering profile on a Cretaceous pluton in a Mediterranean climate (Fig. 2).

## The Pluton

The ~ 95 Ma La Posta pluton is arranged in four concentric facies and has an areal exposure of 1400 km<sup>2</sup>, making it the largest pluton mapped in the Peninsular Ranges of southern California, U.S.A. (Walawender et al. 1990) (Fig. 2). The four concentric facies include, from rim to core, hornblende-biotite, large-biotite, small-biotite, and muscovite-biotite facies. Compositionally, the pluton ranges from a tonalite along its outer margin to a granodiorite/monzogranite near its core. Contacts between adjacent facies are gradational and overall textures are hypidiomorphic granular. Developed on the western part of the pluton is a mantle of loamy coarse sandy soil (Bowman 1973). Pebbly to coarse sandy grus has accumulated on the eastern part.

## The Climate

The La Posta pluton is transected by Mediterranean (hot summer), Mediterranean (cool summer), semiarid, and arid climatic belts (Eidemiller and

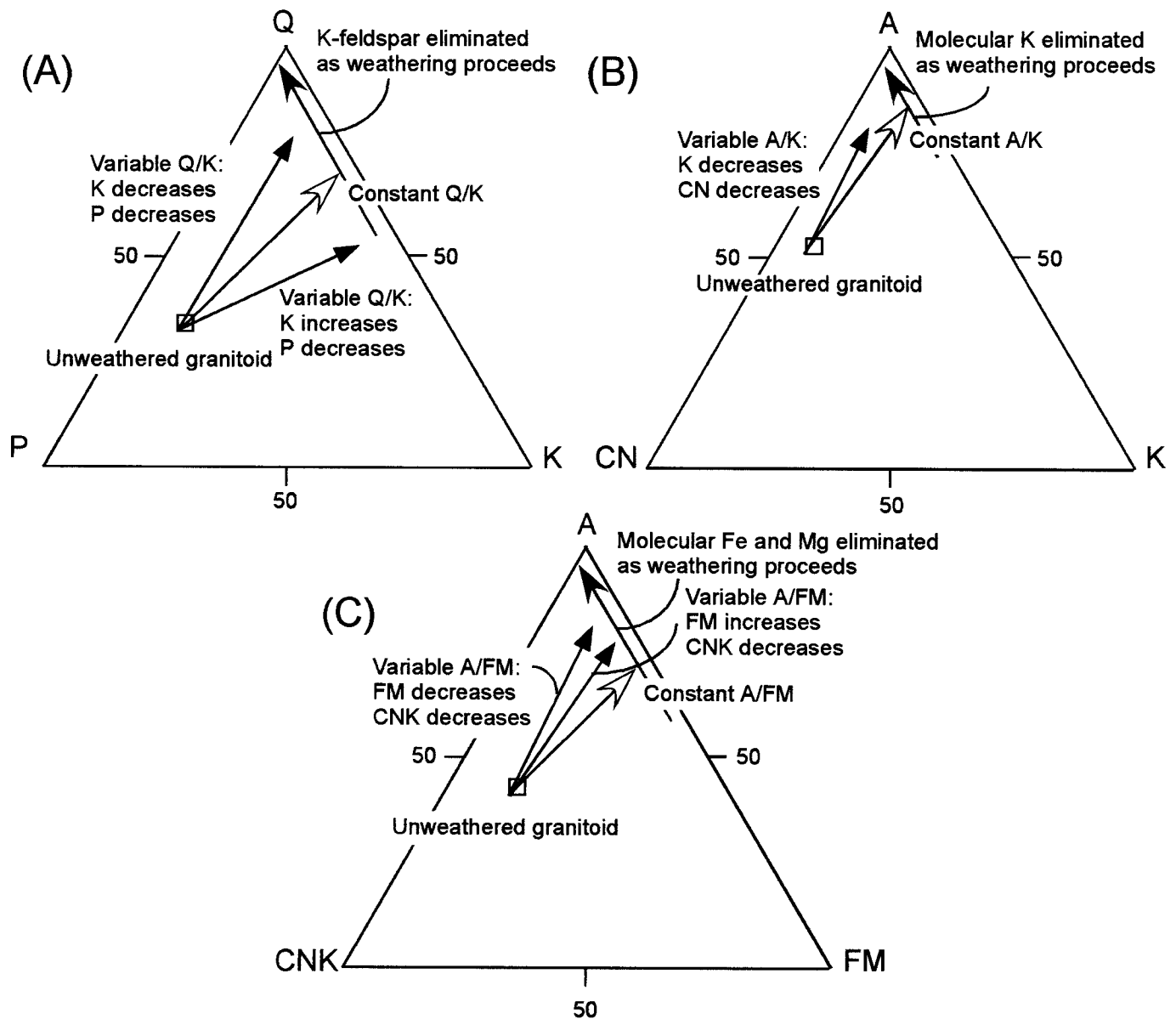


FIG. 1.—Mineralogical and chemical trends predicted by the weathering model of Nesbitt et al. (1996). A) Modal QPK. Q = quartz, P = plagioclase, and K = K-feldspar. B) Molecular A-CN-K. A =  $\text{Al}_2\text{O}_3$ , CN =  $\text{CaO} + \text{Na}_2\text{O}$ , and K =  $\text{K}_2\text{O}$ . C) Molecular A-CN-K-FM. A =  $\text{Al}_2\text{O}_3$ , CNK =  $\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ , and FM =  $\text{FeO} + \text{MgO}$ . Note that for B) and C) data should be corrected for the presence of apatite prior to plotting.

Finch 1972) (Fig. 2). The weathering profile investigated during this study is located within the Mediterranean (hot summer) climatic belt (Fig. 2). Precipitation within the Mediterranean (hot summer) climatic belt is characterized by 38 to 51 cm of annual rainfall, with no more than 3 cm of precipitation occurring during the driest summer month (Eidemiller and Finch 1972; Bowman 1973; Trewartha and Horn 1980). The mean annual air temperature is between  $13.3^\circ\text{C}$  and  $14.4^\circ\text{C}$ , and the frost-free season is 160 to 190 days (Bowman 1973).

As noted later in this paper, the weathering profile that we sampled lies within the La Posta Series loamy coarse sand unit of Bowman (1973). This unit developed on slopes with 5 to 30% grades. Given the active plate boundary setting of the Peninsular Ranges, it is unlikely that such soils could remain in place for any great length of time under such conditions. Hence, we assume that the weathering profile that we studied developed in the Holocene, and that the modern day climatic conditions are likely rep-

resentative of the general conditions under which it developed. Such an interpretation is implied by pedological data provided by Bowman (1973).

### The Weathering Profile

The study site, an  $\sim 4.85$  m high road cut through the apex of a low-lying NS-trending ridge along old Interstate 8, is located within the small-biotite facies of the La Posta pluton at an elevation of 1195 m (3920 feet) (Fig. 2). The land surface of the weathering profile is rocky and slopes gently towards the road cut exposing the weathering profile. Vegetation is dominated by chamise but also includes red shank and annual grasses (cf. Bowman 1973). The sampling site was selected because of its accessibility and the generally well-developed character of the prominent weathering horizons described below (Fig. 3).

Two crudely developed joint sets are visible in the studied outcrop. One

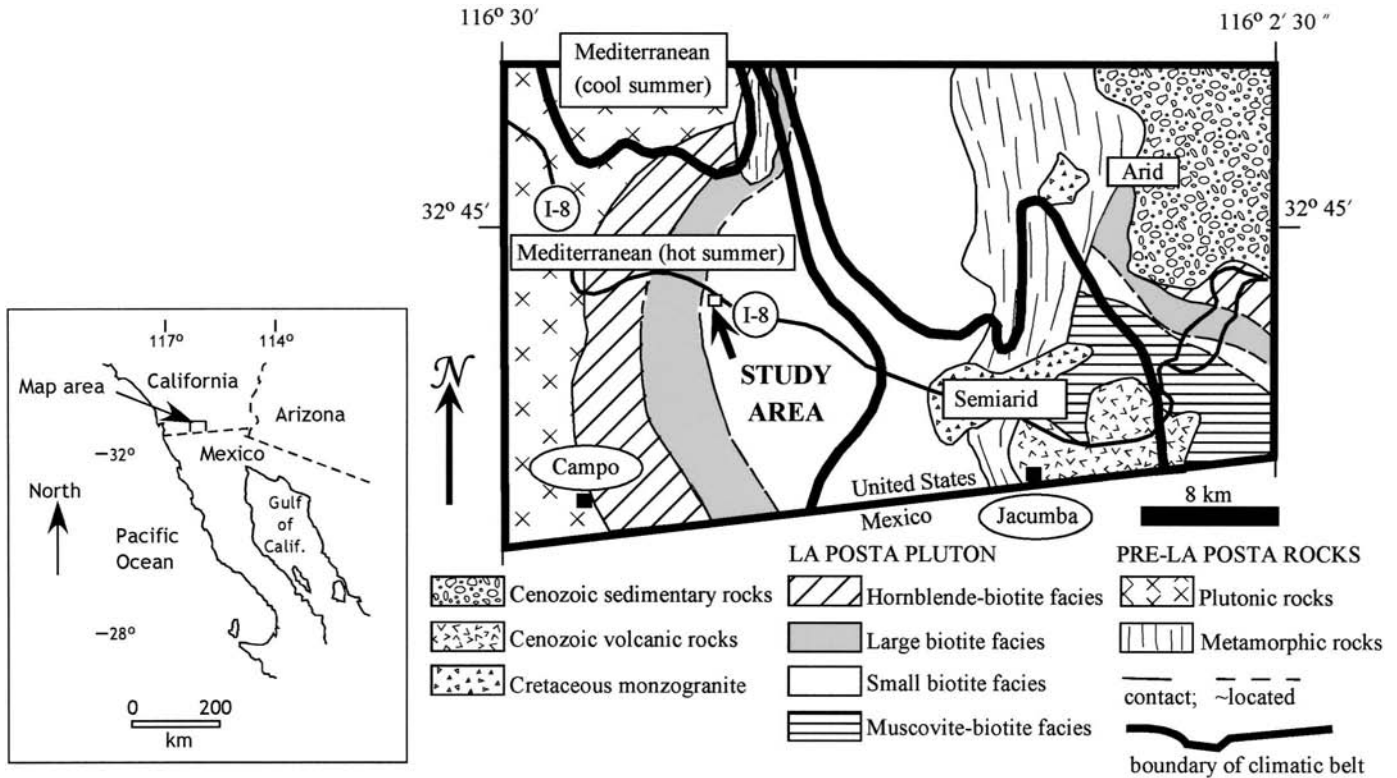


FIG. 2.—Generalized geologic map showing the location of the study site in a Mediterranean (hot summer) climate.

set is subhorizontal and widely spaced (i.e.,  $\sim 2$  m spacing between individual joints). The other set strikes between  $N40^{\circ}E$  and  $N50^{\circ}E$ , and dips between  $55^{\circ}$  and  $65^{\circ}$  NE. The spacing of joints within the NE-striking joint set varies from about 30 cm to as much as 3 to 5 m. Obvious joint surfaces were avoided during sampling.

Relatively unweathered granitoid forms the base of the weathering profile, and is composed of light gray to yellowish/orange (8YR 5/4) hypidiomorphic granular granodiorite (Fig. 3). When struck with a rock hammer the granodiorite produces a “ringing” sound, and the hammer rebounds readily. Millimeter-thick red iron oxide rinds typical of the overlying friable granodiorite are not as well developed within the unweathered granodiorite or are absent.

Unweathered granodiorite grades across an irregular diffuse and wavy boundary into an overlying horizon,  $\sim 1.97$  m in thickness, composed of pitted, very friable, and soft moderate brown (5YR 4/4) to moderate yellow/brown (10YR 5/4) granodiorite (Fig. 3). When struck with a rock hammer, the horizon of friable granodiorite breaks and crumbles easily, the impact producing a “thump” sound. In addition, grains and fragments are readily plucked from the horizon of friable granodiorite by the movement of the hand over its exposed surface. Thin millimeter-thick red iron oxide halos surrounding biotite grains are evident throughout the horizon of friable granodiorite.

Above the friable granodiorite is  $\sim 0.91$  m of gray/orange (10YR 7/4) to pale yellow/orange (10YR 2/6) very coarse loamy sand with scattered pebbles (Fig. 3). The very coarse loamy sand is poorly sorted, massive, very friable, and weakly indurated. When struck with the hammer it readily disaggregates.

Throughout the very coarse loamy sand are partially disaggregated irregularly shaped masses of the underlying friable granodiorite. Some of these masses appear to extend from the underlying horizon of friable granodiorite (Fig. 3). Contacts between such extensions and the enclosing very coarse loamy sand appear irregular and diffuse.

Bleached loamy sand was observed as a rind  $\sim 2$  to  $\sim 3$  cm thick around some roots of chamise that extended from the surface downward into the horizons of very coarse loamy sand and friable granodiorite. None of the samples collected from these horizons included such rinds.

The weathering profile described above lies within the La Posta Series loamy coarse sand unit of Bowman (1973). Soil within this unit lacks well-developed horizons of translocated clay, and belongs to the order Mollisol, subgroup Entic Haploxerolls (Bowman 1973). The loamy coarse sand unit is generally characterized by (1) a variable thick  $C_r$  horizon consisting of weathered granodiorite that retains the mineralogical and textural aspects of the underlying parent material in the R horizon (terminology after Birke-land (1999)), (2) an overlying  $\sim 25$ – $74$  cm thick C horizon composed of loamy coarse sand derived from the underlying weathered granodiorite, and (3) a capping thin ( $\sim 20$ – $25$  cm thick) organic-rich A horizon that is slightly acidic (Bowman 1973). For a comprehensive description of the morphological properties of the La Posta Series soils see Bowman (1973).

Though the A horizon was not present in the vertical section that we sampled, the relatively unweathered granodiorite, friable granodiorite, and very coarse loamy sand studied during this investigation probably corresponds to the R,  $C_r$ , and C horizons, respectively, of the loamy coarse sand unit of Bowman (1973). The absence of the A horizon in the studied profile is not surprising, in as much as the La Posta loamy coarse sand unit developed on slopes with 5% to 30% grades and is characteristically strongly dissected (Bowman 1973).

#### METHODOLOGY

Four samples of the unweathered granodiorite, eight samples from the friable granodiorite, and six samples from the very coarse loamy sand were collected for thin-section and chemical analyses. Samples from the very coarse loamy sand were collected at  $\sim 15$  cm intervals below the top of the exposed portion of the weathering profile, and specimens from the

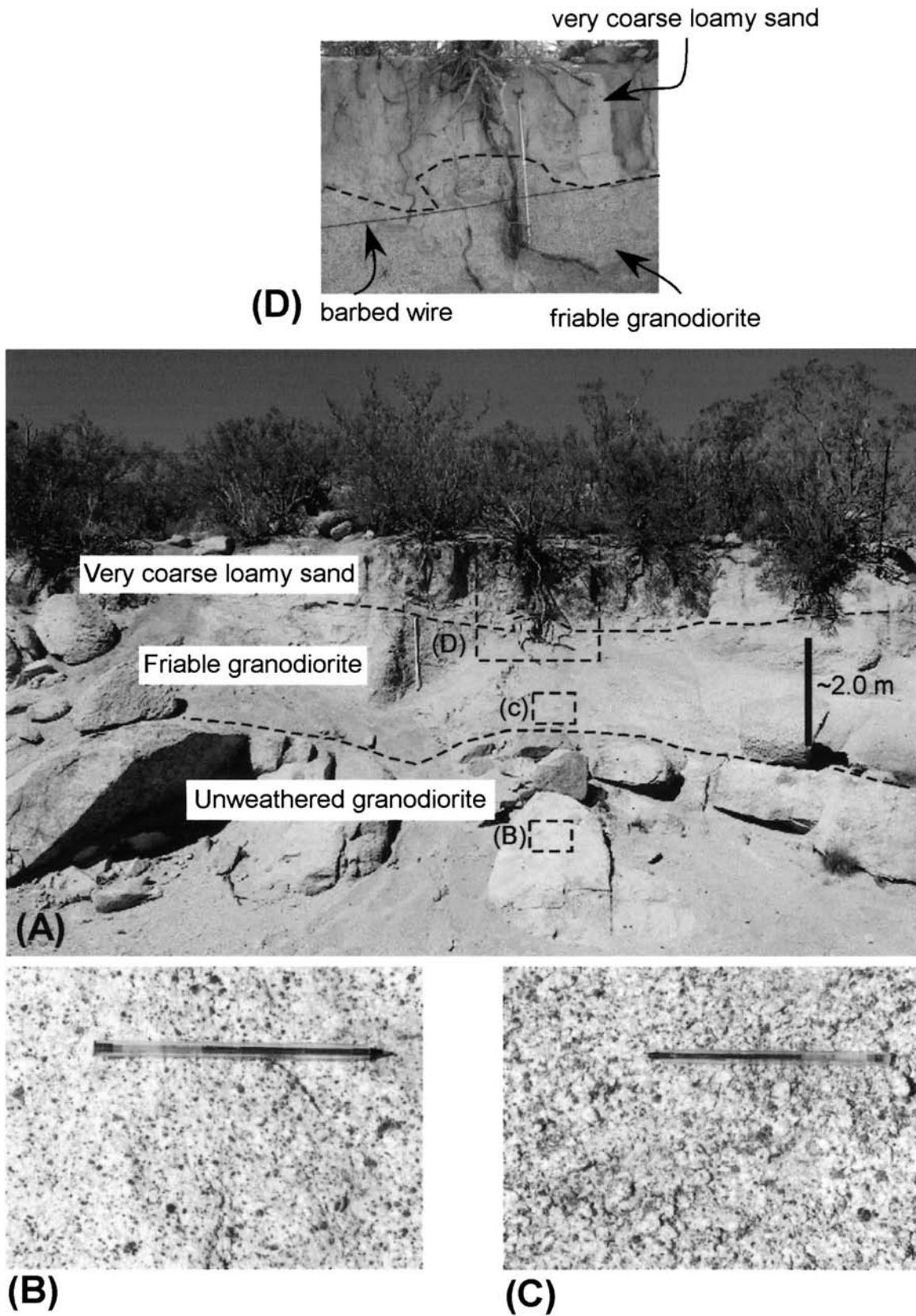


FIG. 3.—A) Photograph of studied weathering profile. Small dashed squares are the locations of photographs labeled (B), (C), and (D). B) Close-up view of unweathered granodiorite. C) Close-up view of friable granodiorite. D) View of contact between very coarse loamy sand and underlying friable granodiorite. Pen in B and C is 15 cm long. Jacob's staff in D is ~ 1 m in length. Most of the plants and associated root structures visible in A are chamise.

TABLE 1.—Summary of 1000 bootstraps of point-count data<sup>1</sup>

	Quartz	Plagioclase	K-feldspar	Biotite	Hornblende	Titanite	Chlorite
Very coarse loamy sand							
Mean	44.3	26.7	10.3	18.0	0.6	0.1	0.0
2.5 percentile	41.9	24.4	9.3	16.9	0.4	0.0	0.0
97.5 percentile	46.6	29.0	11.4	19.1	0.7	0.2	0.1
Friable granodiorite							
Mean	30.6	43.0	9.7	16.0	0.5	0.2	0.1
2.5 percentile	29.2	41.3	8.8	14.9	0.3	0.1	0.0
97.5 percentile	32.1	44.5	10.6	17.0	0.7	0.2	0.1
Unweathered granodiorite							
Mean	28.8	50.2	11.3	9.2	0.3	0.2	0.1
2.5 percentile	27.7	48.7	9.7	8.3	0.1	0.1	0.0
97.5 percentile	29.8	51.7	13.0	10.0	0.6	0.3	0.3

<sup>1</sup> Each sample was point counted 8 times. Point counters were G.H. Girty, J. Marsh, A.J. Meltzner, J.R. McConnell, D. Nygren, G. Prince, and K. Randall. Resulting data were then randomly sampled with replacement following the sampling algorithm discussed in Ague and van Haren (1996) and Girty and Lawrence (2000). From the resulting bootstraps the 2.5 and 97.5 percentiles were calculated.

horizon of friable granodiorite were collected at ~ 25 cm intervals. Two specimens were extracted at each sampling level. One sample was used for thin sectioning, and the other for chemical analysis. All four samples of the unweathered granodiorite were collected from near the base of the exposed weathering profile within an ~ 1.5 m<sup>2</sup> area.

Specimens (~ 100 to 150 grams/sample) from the unweathered granodiorite were hammered from the outcrop. In contrast, specimens from the friable granodiorite and very coarse loamy sand were collected in clean plastic vials (~ 5 cm long with an ~ 2.5 cm diameter). Prior to collection ~ 10–20 cm of the surface was scrapped off and blown clean. The long dimension of the sampling vial was then inserted into the cleaned surface with a twisting coring-like motion.

Samples collected from the very coarse loamy sand and friable granodiorite were consolidated with epoxy resin prior to thin sectioning. All thin sections were of standard size (45 mm × 25 mm) and were chemically stained to distinguish K-feldspar from plagioclase. Point-count spacing was set so that no grain was counted twice. As a result, the number of points counted varied from 113 to 223, with the majority ranging between 160 and 220. In order to average out personal bias during counting, each investigator ( $n = 8$ ), with the exception of D. Johnson, B. Heitman, and J. Nielsen, point counted each sample. The resulting data were used to assess the relative percentages of the major mineralogical components quartz (Q), plagioclase (P), K-feldspar (K), biotite, hornblende, titanite, and chlorite (Table 1). To improve estimates of the averages of QPK components an additional investigator (J. Nygren) was added for a total of nine point counters per sample (Table 2). Averages and the 2.5 and 97.5 percentiles (i.e., 95% confidence intervals) were determined utilizing a bootstrap program written by B. Heitman and G.H. Girty. The bootstrap technique is a nonparametric Monte Carlo statistical technique popularized by Efron and Tibshirani (1993). Resulting averages and statistical uncertainties are summarized in Tables 1 and 2.

All chemical analyses were completed by D. Johnson in the Geo-Analytical Laboratory of Washington State University, Pullman, Washington, and are listed in Table 3. Single 2:1 lithium tetraborate/rock-powder fused disks of each sample were analyzed for major elements and some trace elements following conventional X-ray fluorescence (XRF) techniques on an automatic Rigaku 3370 spectrometer (Hooper et al. 1993). Approximately 25–30 grams of sample was used to produce the powders for the fused disks. Each elemental analysis was fully corrected for line interference and matrix effects. Loss on ignition was not determined, and therefore all chemical arguments presented here bear on changes in elemental mass other than those contributed by changes in volatile components such as H<sub>2</sub>O. Total iron is expressed as FeO. Repeated analysis of well-characterized standards suggests that precisions for major-element data, as measured by one-standard-deviation values, are < 1 relative percent, whereas precisions for trace-element data are less than ~ 5–20 rel-

TABLE 2.—Summary of 2000 bootstraps of QPK components<sup>1</sup>

Samples	Quartz	2.5/97.5 Percentiles	Plagioclase	2.5/97.5 Percentiles	K-feldspar	2.5/97.5 Percentiles
Very coarse loamy sand						
1	52.3	46.5/58.0	37.5	31.2/43.7	10.2	8.7/11.8
2	48.7	44.0/52.9	37.7	32.5/43.0	13.7	11.6/15.6
3	59.5	52.6/66.3	23.6	18.0/30.5	16.8	13.3/21.0
4	56.1	52.3/60.2	34.9	31.1/38.6	9.0	7.5/10.4
5	50.0	45.4/54.3	34.6	29.0/40.4	15.4	11.9/19.5
6	52.4	45.8/58.8	32.6	26.4/39.2	15.0	12.7/17.7
Friable granodiorite						
7	37.3	34.0/40.4	54.2	51.4/57.0	8.5	7.3/10.3
8	33.7	28.0/38.4	56.4	53.5/59.2	9.9	6.5/14.1
9	35.2	32.6/37.5	52.3	49.2/55.2	12.6	11.0/14.0
10	26.8	22.3/32.0	56.7	50.7/61.5	16.6	14.7/19.0
11	40.1	33.8/46.1	46.5	41.4/52.1	13.4	11.5/15.2
12	37.5	33.1/41.4	47.6	44.3/51.2	14.9	12.7/16.9
13	37.6	33.0/42.8	49.6	44.5/54.2	12.8	10.5/15
14	38.1	35.4/41.0	52.3	48.4/55.5	9.6	6.9/12.7
Unweathered granodiorite						
15	31.4	30.0/32.7	54.6	52.4/56.7	14.0	11.3/16.6
16	34.0	31.6/36.7	57.0	55.0/58.4	9.0	6.9/10.7
17	31.1	29.9/32.5	58.4	56.4/60.7	10.4	8.0/12.4
18	32.8	30.0/35.9	52.1	49.4/55.0	15.1	10.5/18.9

<sup>1</sup> Each sample was point counted 9 different times. Point counters were G.H. Girty, J. Marsh, A.J. Meltzner, J.R. McConnell, D. Nygren, J. Nygren, G. Prince, and K. Randall. Resulting data were then randomly sampled with replacement following the sampling algorithm discussed in Ague and van Haren (1996) and Girty and Lawrence (2000). From the resulting bootstraps the 2.5 and 97.5 percentiles were calculated.

ative percent, depending upon the analyzed trace element and its concentration (Hooper et al. 1993). Chemical data are provided in Table 3.

## PETROLOGICAL CHARACTERISTICS

### Unweathered Granodiorite

On average, samples collected from the unweathered granodiorite are composed of ~ 28% quartz, ~ 50% plagioclase, ~ 11% K-feldspar, ~ 9% biotite, and trace amounts (< 1%) of hornblende, titanite, and chlorite (Table 1). These mineralogical components are arranged in a hypidiomorphic granular texture with interstitial irregular shaped pockets of anhedral undulatory to non-undulatory quartz and K-feldspar reaching up to ~ 1 cm in size.

Within the unweathered granodiorite plagioclase, ranging in size from ~ 0.2 mm by ~ 0.4 mm to ~ 1.5 mm by ~ 2.4 mm, is subhedral to euhedral. Most plagioclase crystals display polysynthetic twins, and are concentrically zoned with slightly more An-rich cores (Walawender et al. 1990). White mica and epidote are local replacement products of plagioclase cores.

Anhedral to subhedral biotite is a ubiquitous constituent in samples studied from the unweathered granodiorite. It characteristically ranges in size from ~ 0.15 mm by ~ 0.2 mm to ~ 2.0 mm by ~ 4.0 mm and exhibits a deep red to brown pleochroism. Locally biotite is altered along cleavage planes to “berlin-blue” chlorite.

In samples from the unweathered granodiorite, subhedral hornblende ranges in size from ~ 0.3 mm by ~ 0.4 mm to ~ 2.2 mm by ~ 2.8 mm. It displays a dark green to light green pleochroism and the characteristic cleavage typical of the amphibole group. Other trace minerals include euhedral to subhedral titanite (< ~ 0.15 mm by ~ 0.5 mm to ~ 0.9 mm by ~ 2.6 mm in size) and apatite (< 0.01 mm by ~ 0.03 mm in size). The latter mineral is an inclusion in both biotite and feldspar.

### Friable Granodiorite

The average composition of specimens from the friable granodiorite is ~ 31% quartz, ~ 43% plagioclase, ~ 10% K-feldspar, ~ 16% biotite, and trace amounts of hornblende, titanite, and chlorite (Table 1). Titanite (≤ ~ 0.4 mm by ~ 1.3 mm in size) is altered to a black opaque cryptocrystalline phase, whereas quartz (~ 0.05 mm by ~ 0.1 mm to ~ 0.8 mm by ~ 1.2 mm in size), K-feldspar (~ 0.15 mm by ~ 0.15 mm to ~

TABLE 3.—Summary of chemical data

Sample #	1LS <sup>1</sup>	2LS	3LS	4LS	5LS	6LS	7FG <sup>2</sup>	8FG	9FG	10FG	11FG	12FG	13FG	14FG	15UG <sup>3</sup>	16UG	17UG	18UG
Weight % <sup>4</sup>																		
SiO <sub>2</sub>	69.3	69.7	69.1	69.7	68.6	69.3	69.8	70.2	70.3	70.2	70.3	70.8	68.8	70.4	70.8	71.4	70.9	71.1
Al <sub>2</sub> O <sub>3</sub>	17.0	17.0	17.4	17.0	17.8	17.4	16.0	16.1	16.3	16.6	16.0	15.7	15.7	15.7	15.7	15.3	15.7	15.9
TiO <sub>2</sub>	0.64	0.60	0.67	0.59	0.64	0.66	0.57	0.49	0.51	0.51	0.60	0.53	0.67	0.57	0.50	0.51	0.48	0.46
FeO <sup>5</sup>	2.96	2.70	2.90	2.71	2.98	3.00	2.64	2.27	2.38	2.30	2.68	2.32	2.99	2.59	2.15	2.21	2.22	1.98
MnO	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.05	0.05	0.06	0.05	0.04	0.04	0.04	0.04
CaO	2.45	2.40	1.78	2.33	2.10	1.90	3.15	3.22	3.20	3.02	3.11	3.22	3.38	3.25	3.41	3.20	3.41	2.48
MgO	1.00	0.93	0.86	0.92	0.96	0.92	1.00	0.85	0.85	0.78	0.94	0.87	1.13	0.89	0.84	0.80	0.83	0.79
K <sub>2</sub> O	2.23	2.08	2.33	2.29	2.09	2.27	1.90	1.99	1.93	1.97	1.89	1.95	2.10	2.03	2.32	2.42	2.27	2.27
Na <sub>2</sub> O	2.91	2.93	2.40	2.81	2.60	2.39	3.60	3.81	3.84	3.72	3.61	3.77	3.39	3.75	4.00	4.03	4.06	4.12
P <sub>2</sub> O <sub>5</sub>	0.04	0.03	0.03	0.03	0.03	0.02	0.13	0.11	0.13	0.10	0.08	0.11	0.14	0.13	0.13	0.13	0.13	0.13
ppm																		
Ba	764	665	848	754	720	773	550	656	590	721	674	580	854	588	941	815	797	818
Rb	69	64	68	71	64	65	62	60	66	71	71	64	74	65	66	69	64	63
Sr	343	349	304	343	328	311	418	439	433	421	455	433	444	435	478	460	534	486
Zr	144	142	138	147	141	144	132	121	130	127	133	132	143	126	123	123	127	120
Y	11	11	8	8	10	7	11	10	12	12	18	10	14	14	9	11	6	6
Ga	24	20	22	22	21	23	20	19	21	19	20	18	19	20	18	18	22	19
Zn	69	62	62	70	66	66	78	71	71	73	72	70	89	72	69	66	70	68
Pb	16	19	15	16	15	16	14	16	14	17	16	13	16	14	13	15	19	17
Th	9	6	8	12	7	6	2	2	8	4	23	2	4	4	2	7	2	10

<sup>1</sup> LS designates sample from very coarse loamy sand.

<sup>2</sup> FG designates sample from friable granodiorite.

<sup>3</sup> UG designates sample from unweathered granodiorite.

<sup>4</sup> Data are un-normalized.

<sup>5</sup> Total iron expressed as FeO.

0.7 mm by ~ 1.5 mm in size), and hornblende (~ 0.15 mm by ~ 0.2 mm to ~ 0.6 mm by ~ 1.2 mm in size) appear to have been unaffected by chemical weathering. In contrast, about 55% of the observed plagioclase grains (~ 0.1 mm by ~ 0.2 mm to ~ 0.8 mm by ~ 1.5 mm in size) have more than ~15% of their observed surface area converted to a cryptocrystalline clay material. Alteration of plagioclase is most intense within more An-rich cores but also occurs along fractures and compositional planes and around the edges of individual plagioclase crystals.

Boundaries of individual biotite grains (~ 0.05 mm by ~ 0.2 mm to ~ 2.2 mm by ~ 2.5 mm in size) in the friable granodiorite are characterized by a thin (< ~ 0.01 mm), somewhat corrugated and discontinuous rind composed of a cryptocrystalline nearly opaque red iron oxide phase.

Such material may represent an insoluble residue. The cryptocrystalline iron oxide phase is also present along cleavage planes, and it forms a discontinuous rind around inclusions of apatite, opaque quartz, and plagioclase. In some biotite grains, partial dissolution of apatite inclusions is evident.

**Very Coarse Loamy Sand**

On average, samples from the very coarse loamy sand are composed of ~ 44% quartz, ~ 27% plagioclase, ~ 10% K-feldspar, ~ 18% biotite, and trace amounts of hornblende, titanite, and chlorite (Table 1). In thin sections, sand-size grains are very poorly sorted and mud-size material forms a haphazard mosaic of fragments of biotite, quartz, plagioclase, and K-feldspar partially or wholly encircled by a cryptocrystalline clay material.

Quartz fragments in specimens from the very coarse loamy sand are unaltered, angular to subangular, and undulatory to nonundulatory, and they form the largest crystal fragments (up to ~ 1.5 mm by ~ 2.0 mm in size) in a given sample. In contrast, plagioclase, ranging in size from ~ 0.05 mm by ~ 0.05 mm to ~ 0.9 mm by ~ 1.6 mm, is altered along cleavage and compositional planes, fractures, and in more An-rich cores to a cryptocrystalline clay material. Such alteration makes up greater than ~ 15% of the observed surface area of about 65% of the counted plagioclase grains, leaving plagioclase with a distinctly murky appearance when viewed in plane light.

In the very coarse loamy sand, K-feldspar, ranging in size from ~ 0.05 mm by ~ 0.05 mm to ~ 0.7 mm by ~ 1.0 mm, is subround to subangular whereas subangular hornblende ranges in size from ~ 0.05 mm by ~ 0.05 mm to as large as ~ 0.6 mm by ~ 2.4 mm. Neither K-feldspar nor hornblende display any significant alteration to clay.

Platy biotite grains range in size from ~ 0.02 mm by ~ 0.05 mm to ~ 0.3 mm by ~ 1.4 mm, whereas titanite grains range from ~ 0.2 mm by ~ 0.2 mm to as large as ~ 0.8 mm by ~ 1.5 mm. Alteration of biotite and titanite is similar to that observed in samples from the friable granodiorite. Apatite was not identified with certainty in any of the samples studied from the very coarse loamy sand.

**RESULTS**

**Point Counts**

Point-count results are plotted on a Q-P-K ternary diagram in Figure 4 (see also Table 2). All samples from the unweathered granodiorite, as well

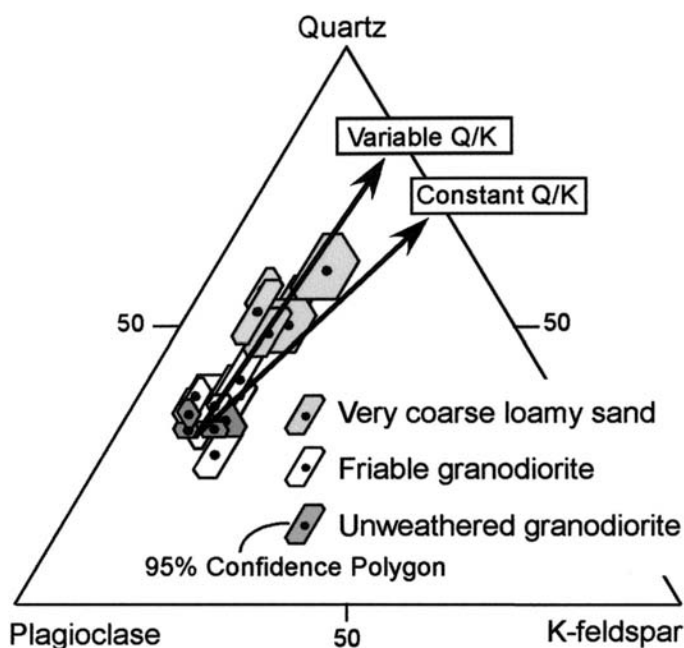


Fig. 4.—Point-count data plotted on a QPK ternary diagram. See caption to Figure 1 for QPK definitions.

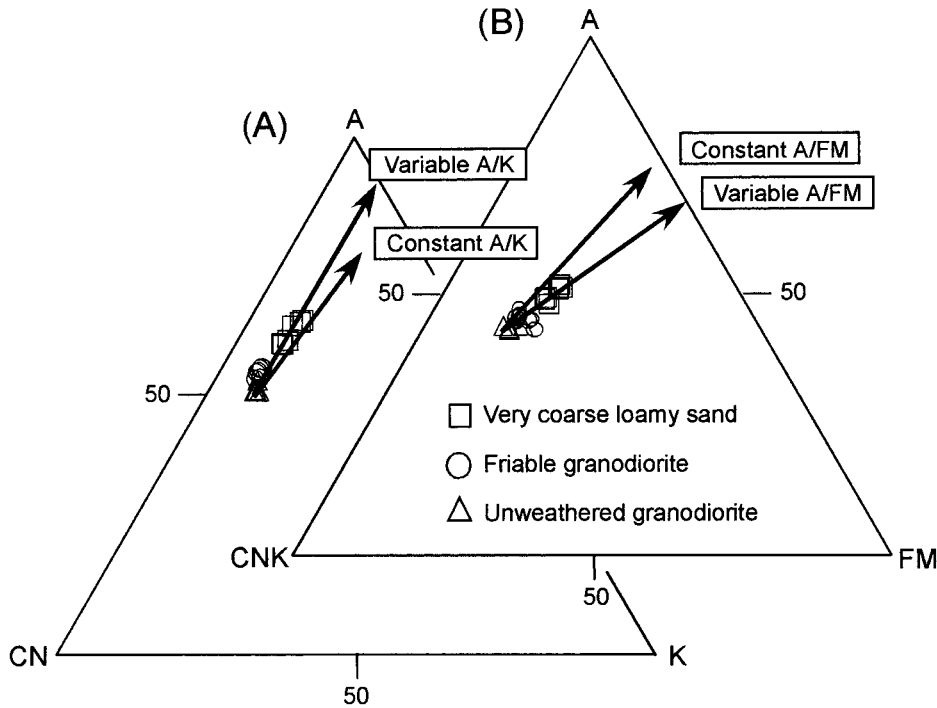


FIG. 5.—Chemical data plotted in the molecular A) A-CN-K and B) A-CN-K-FM ternary systems. See caption to Figure 1 for definitions of A-CN-K and A-CN-K-FM. Note that for A and B data were corrected for the presence of apatite prior to plotting.

as most samples from the friable granodiorite, form a clustering of points. In contrast, a few specimens from the friable granodiorite along with all specimens from the very coarse loamy sand spread from this cluster of data toward the Q-K join. These relationships indicate that both plagioclase and K-feldspar are being leached from the very coarse loamy sand, and to a lesser degree from at least some of the samples from the friable granodiorite. In addition, the fact that the observed trend deviates toward the Q apex and away from the hypothetical constant Q/K weathering trend shown in Figure 4 suggests that plagioclase is being leached at a faster rate than is K-feldspar (cf. Fig. 1A). Such a conclusion is supported by the observation that plagioclase commonly displays the effects of chemical weathering but little clay alteration of K-feldspar was observed during thin section study.

#### Chemical Analyses

Because our sampling procedure avoided material adjacent to roots and joint surfaces, chemical changes described below occurred within the “matrix” of Frazier and Graham (2000). Chemical data are plotted on the molecular A-CN-K ternary diagram in Figure 5A. Prior to plotting, data were corrected for the presence of apatite following the recommendations and procedures of McLennan (1993). Samples from the unweathered granodiorite consistently plot below those from the friable granodiorite whereas the latter samples consistently plot below those analyzed from the very coarse loamy sand. Moreover, data form a trend that is directed toward the A apex, deviating slightly from the weathering trend predicted for a constant A/K ratio (cf. Fig. 1B). This result implies that within the weathering profile Ca and Na are being leached from plagioclase and titanite (and possible hornblende) at a rate faster than K is being leached from K-feldspar and biotite.

On the A-CN-K-FM diagram (Fig. 5B) data form a linear weathering trend directed away from the CNK apex and toward the A-FM join. This trend deviates toward the FM apex and away from the weathering trend characterized by a constant A/FM ratio. Such a relationship suggests that Fe and/or Mg have been added to the very coarse loamy sand, and to a

lesser degree to the friable granodiorite (cf. Fig. 1C). Both Fe and Mg are prevalent cations found in hornblende and biotite.

As mentioned earlier in this report, the A horizon that should have capped the studied weathering profile was likely removed by erosion. Nevertheless, given that under the influence of gravity solutions migrate downward, it appears that, prior to erosion, Fe and/or Mg may have been leached from the A horizon and then were carried to and reprecipitated at deeper levels within both the friable granodiorite and very coarse loamy sand.

In summary, thin-section study along with bulk chemical data indicate that during the development of the very coarse loamy sand and friable granodiorite considerable elemental mass may have been removed. Can mass-balance relationships be used to estimate how much bulk and individual elemental mass was removed to form the studied weathering profile?

#### Estimating Bulk and Elemental Mass Change

The weathering profile studied during this investigation developed *in situ* on the underlying granodiorite. Hence, the composition of the source material is known, and as a result, application of the mass-balance equations and statistical techniques of Brimhall and Dietrich (1987), Woronow and Love (1990), and Ague (1994) to the development of the loamy sand and friable granodiorite is warranted.

In order to apply mass-balance techniques an immobile element must first be identified, i.e., an element whose mass was conserved during the development of the studied weathering profile. Al and Zr are elements with low solubility in common soil solutions and therefore are candidates for the immobile element (Brimhall and Dietrich 1987; Young and Nesbitt 1998; Birkeland 1999). In contrast, though TiO<sub>2</sub> is often used in mass-balance studies, textural data described earlier in this paper indicate that the principal Ti-bearing mineral, titanite, was extensively attacked and altered by soil solutions within the friable granodiorite and very coarse loamy sand. In addition, Hamdan and Burnham (1996) rank Ti as being more mobile than Al during pedogenesis of granite. Hence, TiO<sub>2</sub> was not considered to be a viable candidate for the immobile element.

A bivariate plot of the concentrations of Al<sub>2</sub>O<sub>3</sub> and Zr is shown in Figure

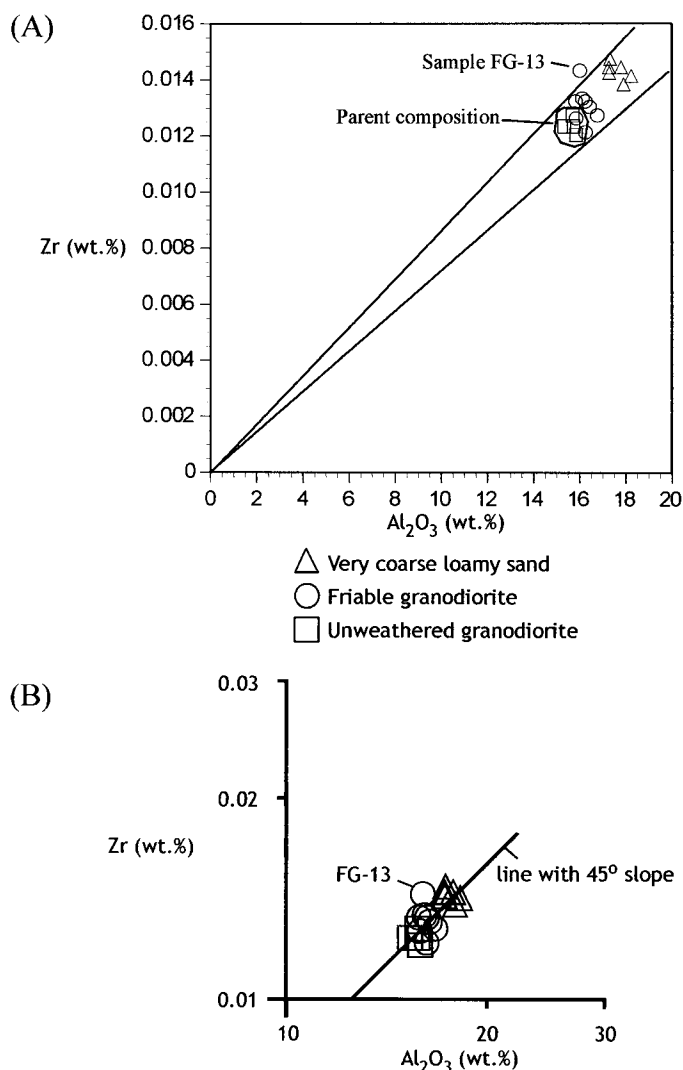


FIG. 6.—A) A bivariate plot of Zr versus Al<sub>2</sub>O<sub>3</sub> concentrations. B) Log-log plot of Zr versus Al<sub>2</sub>O<sub>3</sub> concentrations.

6A. On this diagram all but one sample from the very coarse loamy sand and friable granodiorite plot within the cone defined by two lines emanating from the origin and passing tangentially to the compositional field defined by specimens analyzed from the unweathered granodiorite. The one anomalous sample appears to have a slightly higher concentration of Zr than expected. This result may be the result of a heterogeneous distribution of zircon, the principal mineral containing Zr, or it may be an effect of an imprecise analytical determination. Because of these uncertainties the anomalous sample is hereafter treated as a statistical outlier. However, including it in the following mass balance arguments would not significantly alter our final conclusions.

If the interpretation that Al<sub>2</sub>O<sub>3</sub> and Zr were immobile during development of the weathering profile is correct, then on a log-log plot data should cluster about a line with a 45° slope (S.R. McLennan, personal communication 2002). As shown in Figure 6B, all chemical data from the weathering profile follow this pattern. Hence, the use of either of these two elements as the immobile species is justified.

In Figure 6, samples from the friable granodiorite plot above those from the unweathered granodiorite and below those analyzed from the very coarse loamy sand. These relationships are consistent with the residual enrichment model of Ague (1994) and suggest that the loamy sand under-

TABLE 4.—Estimates of bulk and elemental mass change

	Percent Change UG - FG <sup>1</sup>			Percent Change UG - LS <sup>1</sup>		
	Mean	Minimum <sup>3</sup>	Maximum <sup>3</sup>	Mean	Minimum <sup>3</sup>	Maximum <sup>3</sup>
Change in Bulk Mass <sup>2</sup>						
Al <sub>2</sub> O <sub>3</sub>	-3.4	-1.4	-5.5	-11.2	-9.1	-13.3
Zr	-4.3	-1.0	-7.6	-13.6	-11.1	-16.1
Change in Elemental Mass <sup>4</sup>						
SiO <sub>2</sub>	-3.7	-0.8	-6.5	-11.7	-8.7	-14.6
Al <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0
TiO <sub>2</sub>	7.4	20.2	-4.1	16.7	25.6	8.4
FeO	11.5	24.1	0.1	21.6	31.0	12.8
MnO	6.6	23.6	-8.0	-12.3	-5.3	-18.8
CaO	-8.6	-3.7	-13.3	-42.4	-32.7	-50.8
MgO	5.4	17.5	-5.5	3.3	11.0	-3.9
K <sub>2</sub> O	-18.1	-13.7	-22.3	-13.6	-6.8	-19.9
Na <sub>2</sub> O	-10.5	-7.1	-13.7	-40.5	-33.3	-46.9
P <sub>2</sub> O <sub>5</sub>	-16.7	-2.6	-28.8	-79.6	-74.9	-83.4
Ba	-28.8	-19.8	-36.7	-20.6	-11.1	-29.1
Zr	0.8	6.5	-4.6	2.8	8.5	-2.6
Ga	-1.6	8.2	-10.4	1.7	14.4	-9.7
Zn	2.5	7.1	-2.0	-14.4	-8.6	-19.9
Th	-0.5	249.3	-71.7	68.4	573.5	-57.9
Y	52.3	117.3	6.8	3.8	50.4	28.4
Pb	-9.8	6.4	-23.5	-9.7	9.3	-25.3
Rb	-3.4	4.8	-11.0	-9.4	-1.5	-16.7
Sr	-14.4	-8.5	-19.9	-40.2	-33.7	-46.0

<sup>1</sup> UG = unweathered granodiorite. FG = friable granodiorite. LS = loamy sand.

<sup>2</sup> Estimates based on equation (1) assuming conservation of Al and Zr mass.

<sup>3</sup> Based on 95% confidence interval.

<sup>4</sup> Estimates based on equations (2) and (3), assuming conservation of Al mass.

went a greater overall loss of bulk mass than did the friable granodiorite. The change in bulk mass, *T*, can be estimated from the relationship

$$T = [C_i^o/C_i^f - 1] * 100 \quad (1)$$

where *C<sub>i</sub><sup>o</sup>* and *C<sub>i</sub><sup>f</sup>* are the concentrations of some immobile element in the original and weathered material, respectively (e.g., Brimhall and Dietrich 1987; Ague 1994). For Al<sub>2</sub>O<sub>3</sub> the above equation yields a value of -3.4% ± 2.0% (2 standard errors) for the friable granodiorite and -11.2% ± 2.1% for the loamy sand (Table 4). If Zr is selected for the framework element, then *T* is -4.3% ± 3.3% for the friable granodiorite and -13.6% ± 2.5% for the very coarse loamy sand (Table 4). Similar results are obtained if data are transformed into the log-ratio format advocated by Aitchison (1986), Ague (1994), and Cardenas et al. (1996).

Woronow and Love (1990) showed that, once an immobile element is selected, the percentage change in any elements mass can be calculated from the relationship

$$\Delta\%mass = 100(e^{\ln f_m} - 1) \quad (2)$$

where

$$\ln(f_m) = \ln(x'_m/x'_{im}) - \ln(x_m/x_{im}). \quad (3)$$

In the above equations *f<sub>m</sub>* is the factor by which the mass of a given element changed, and *x'<sub>m</sub>*, *x'<sub>im</sub>*, *x<sub>m</sub>*, *x<sub>im</sub>* are the concentrations of the mobile element (subscript *m*) and immobile element (subscript *im*) in the parent (unprimed) and altered material (primed), respectively.

The Matlab 5 program Statistical Analysis of Compositional Data (Warren and Girty 1999), based on the equations of Woronow and Love (1990), was used to calculate the percent change in the mass of individual elements and to evaluate statistical uncertainties. The results of this phase of our study are listed in the lower part of Table 4 and are graphically portrayed in Figure 7. In the latter illustration, if the 95% confidence bar does not cross a 0% change in elemental mass, then the results are statistically significant, i.e., there are no statistical data favoring the null hypothesis, *H<sub>o</sub>*, that  $\mu_1 - \mu_0 = 0$  over the alternative hypothesis, *H<sub>a</sub>*, that  $\mu_1 - \mu_0 \neq 0$ . In other words, *H<sub>o</sub>* is rejected in favor of *H<sub>a</sub>*.

From Figure 7B and Table 4 it should be clear that during development of the friable granodiorite Si, Ca, K, Na, P, Ba, and Sr lost ~ 4%, ~ 9%, ~ 18%, ~ 11%, ~ 17%, ~ 29%, and ~ 14% of their masses, respectively. Offsetting this trend is a gain of ~ 12% and ~ 52% of the elemental masses of Fe and Y. Approximately 99% of the 3.4% loss in original bulk

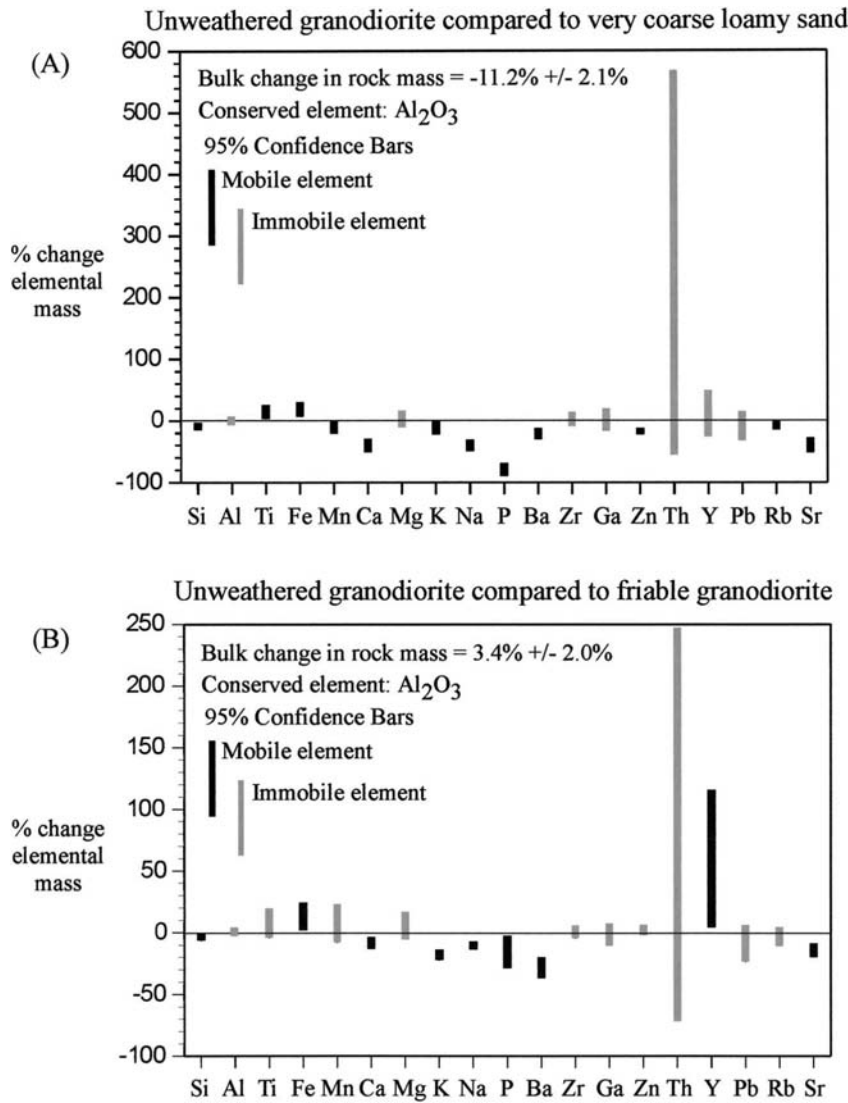


Fig. 7.—Plots of the percent change in elemental mass. **A)** Compares changes from unweathered granodiorite to friable granodiorite. **B)** Compares changes from unweathered granodiorite to very coarse loamy sand. In the GeoAnalytical Laboratory, Washington State University, the detection limit for Th is 1 ppm. The concentration of Th in the studied profile ranges from 2 to 23 ppm (Table 3). Hence, the large confidence bars displayed by Th probably reflect the loss of precision for Th analysis at the low end of this range.

mass of the friable granodiorite is due to the combined losses of Si, Ca, K, and Na mass. These results are consistent with textural data indicating that plagioclase ((Ca, Na)Al<sub>1-2</sub>Si<sub>3-2</sub>O<sub>8</sub>), biotite (K(Fe, Mg)<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(F, O)<sub>2</sub>), apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, Cl)), titanite (CaTiSiO<sub>5</sub>), and possibly K-feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) and hornblende (NaCa<sub>2</sub>(Mg, Fe, Al)<sub>5</sub>(Al, Si)<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>) interacted with soil solutions (generalized chemical formulas from Hurlbut (1971)). Both Ba and Sr are elements that commonly substitute into the feldspar lattice, and their depletion in the very coarse loamy sand and friable granodiorite is likely the result of feldspar dissolution during chemical weathering (Hurlbut 1971; Taylor and McLennan 1985). The addition of Fe and Y to the friable granodiorite may be due to reprecipitation from downward-migrating solutions that attacked biotite within the capping A horizon prior to its removal by erosion.

Thin-section study and bulk chemical data suggest that the more labile minerals (e.g., plagioclase, biotite, titanite, and apatite) in the very coarse loamy sand were attacked more vigorously than those in the friable granodiorite. Hence, it is not surprising that during the development of the very coarse loamy sand, Si, Mn, Ca, K, Na, P, Ba, Zn, Rb, and Sr lost ~ 12%, ~ 12%, ~ 42%, ~ 14%, ~ 41%, ~ 80%, ~ 21%, ~ 14%, ~ 10%, ~ 9%, and ~ 40% of their masses respectively (Fig. 7A; Table 3). In contrast, the masses of Ti and Fe were increased by ~ 17% and ~ 22% respectively. Approximately 99% of the 11.2% bulk mass lost during the

development of the very coarse loamy sand is accounted for by the sum of the losses of Si, Ca, K, and Na mass. As noted above, Ca, Na, Rb, Sr, and Ba are all elements that are common to plagioclase. Ca is also an important cation found in apatite and titanite whereas K is common to both K-feldspar and biotite. Phosphorus (P) and Ca are included in apatite, Fe is housed in biotite, and Ti and Ca are found in titanite. Ca, Na, and Fe are included in hornblende. Though we are uncertain as to which minerals house Mn and Zn, the former element is known to substitute into the amphibole group (Hurlbut 1971). These relationships generally support the idea that in the very coarse loamy sand plagioclase, biotite, titanite, apatite, and possible K-feldspar and hornblende were attacked by soil solutions and were partially dissolved from the weathering profile. In contrast, the apparent enrichment in Ti and Fe in the very coarse loamy sand may be the result of dissolution of titanite and biotite in the capping A horizon prior to its removal by erosion.

#### CONCLUSIONS

Data presented here and elsewhere indicates that weathering profiles developed within a Mediterranean (hot summer) climate are susceptible to significant chemical weathering (e.g., Nettleton et al. 1970; Frazier and Graham 2000). In such an environment, plagioclase, biotite, apatite, and

titanite are significantly degraded while K-feldspar and hornblende are to a lesser degree. As a result, modal and bulk chemical compositions of weathered material in friable granodiorite and very coarse loamy sand are unlike those of the underlying parent granodiorite. This conclusion, and the results of work summarized in Nesbitt et al. (1997), imply that plutonic sediment derived from sources lying within a wide range of climatic conditions, does not reflect directly the bedrock from which they were derived, but instead mirror the compositions of the weathering profile. Though such a conclusion is important, it does not necessarily detract from the importance of plate-tectonic setting as a significant control of terrigenous rock composition (e.g., Dickinson et al. 1983). In fact, it is likely that the modal and chemical compositions of terrigenous rocks, if not severely altered by diagenesis, contain important information about both the long-term intensity of chemical weathering in their provenance, and how the effects of chemical weathering may or may not have been modulated by tectonic activity (McLennan et al. 1993; Johnsson 1993). Clearly, we have much to learn about the effects of chemical weathering and its role in the production of the terrigenous rock system.

#### ACKNOWLEDGMENTS

Work discussed here was funded by a grant from the Petroleum Research Fund to G.H. Girty. The bootstrap and statistical (SACD) programs utilized during this study are freely downloadable at <http://www.geology.sdsu.edu/visualstructure>. We thank reviewers S.M. McLennan and R.C. Graham for their timely and constructive criticism.

#### REFERENCES

- ATCHISON, J., 1986, *The Statistical Analysis of Compositional Data*: London, Chapman & Hall, 416 p.
- AGUE, J.J., 1994, Mass transfer during Barrovian metamorphism of pelites, south-central Connecticut: I. Evidence for changes in composition and volume: *American Journal of Science*, v. 294, p. 989–1057.
- AGUE, J.J., AND VAN HAREN, J.L.M., 1996, Assessing metasomatic mass and volume changes using the bootstrap, with applications to deep crustal hydrothermal alteration of marble: *Economic Geology*, v. 91, p. 1169–1182.
- BIKKELAND, P.W., 1999, *Soils and Geomorphology*: Oxford, U.K., Oxford University Press, 430 p.
- BOETTINGER, J.L., AND SOUTHARD, R.J., 1991, Silica and carbonate sources for aridisols on a granitic pediment, western Mojave Desert: *Soil Science Society of America, Journal*, v. 55, p. 1057–1067.
- BOWMAN, R.H., 1973, *Soil Survey of the San Diego Area, California, Part I: United States Department of Agriculture, Soil Conservation Service and Forest Service*, 104 p.
- BRIMHALL, G.H., AND DIETRICH, W.E., 1987, Constitutive mass balance relations between chemical compositions, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results on weathering and pedogenesis: *Geochimica et Cosmochimica Acta*, v. 51, p. 567–587.
- BUSENBERG, E., AND CLEMENCY, C.V., 1976, The dissolution kinetics of feldspars at 25°C and 1 atm CO<sub>2</sub> partial pressure: *Geochimica et Cosmochimica Acta*, v. 40, p. 41–49.
- CARDENAS, A., GIRTY, G.H., HANSON, A.D., LAHREN, M.M., KNAACK, C., AND JOHNSON, D., 1996, Assessing differences in composition between low metamorphic grade mudstones and high-grade schists using logratio techniques: *Journal of Geology*, v. 104, p. 279–293.
- DICKINSON, W.R., BEARD, L.S., BRAKENRIDGE, G.R., ERJAVEC, J.L., FERGUSON, R.C., INMAN, K.F., KNEPP, R.A., LINDBERG, F.A., AND RYBERG, P.T., 1983, Provenance of North American Phanerozoic sandstones in relation to tectonic setting: *Geological Society of America, Bulletin*, v. 94, p. 222–235.
- DOVE, P.M., AND ELSTON, S.F., 1992, Dissolution kinetics of quartz in sodium chloride solutions: Analysis of existing data and a rate model for 25°C: *Geochimica et Cosmochimica Acta*, v. 56, p. 4147–4156.
- DREYER, J.J., 1988, *The Geochemistry of Natural Waters*: Englewood Cliffs, New Jersey, Prentice-Hall, 437 p.
- ERFON, B., AND TIBSHIRANI, R.J., 1993, *An Introduction to the Bootstrap*: New York, Chapman & Hall, 436 p.
- EIDEMILLER, D.I., AND FINCH, W.A., 1972, *Field trip guide, San Diego County*: San Diego State University, Department of Geography, 54 p.
- FRAZIER, C.S., AND GRAHAM, R.C., 2000, Pedogenic transformation of fractured granitic bedrock, southern California: *Soil Science Society of America, Journal*, v. 64, p. 2057–2069.
- GIRTY, G.H., AND LAWRENCE, J.L., Bootstrap technique and the location of the source of siliciclastic detritus in the lower Paleozoic Shoo Fly Complex, northern Sierra terrane, California, in Soreghan, M.J., and Gehrels, G.E., eds., *Paleozoic and Triassic paleogeography and tectonics of western Nevada and northern California*: Boulder, Colorado, Geological Society of America, Special Paper 347, p. 173–184.
- HAMDAN, J., AND BURNHAM, C.P., 1996, The contribution of nutrients from parent material in three deeply weathered soils of Peninsular Malaysia: *Geoderma*, v. 74, p. 219–233.
- HOLDREN, G.R., AND SPEYER, P.M., 1985, Reaction rate–surface area relationships during the early stages of weathering—I. Initial observations: *Geochimica et Cosmochimica Acta*, v. 49, p. 675–681.
- HOLDREN, G.R., AND SPEYER, P.M., 1987, Reaction rate–surface area relationships during the early stages of weathering—II. Data on eight additional feldspars: *Geochimica et Cosmochimica Acta*, v. 51, p. 2311–2318.
- HOOPER, P.R., JOHNSON, D., AND CONREY, R.M., 1993, *Major and trace element analysis of rocks and minerals by automated X-ray spectrometry*: Pullman, Washington, Washington State University, Department of Geology, Open File Report, 36 p.
- HURLBUT, C.S., 1971, *Dana's Manual of Mineralogy*: New York, John Wiley & Sons, 579 p.
- JOHNSON, M.J., 1993, The system controlling the composition of clastic sediments, in Johnsson, M.J., and Basu, A., eds., *Processes Controlling the Composition of Clastic Sediments*: Geological Society of America, Special Paper 284, p. 1–19.
- JONES, D.P., AND GRAHAM, R.C., 1993, Water-holding characteristics of weathered granitic rock in chaparral and forest ecosystems: *Soil Science Society of America, Journal*, v. 57, p. 256–261.
- MAST, M.A., AND DREYER, J.J., 1987, The effect of oxalate on the dissolution rates of oligoclase and tremolite: *Geochimica et Cosmochimica Acta*, v. 51, p. 2559–2568.
- MCLENNAN, S.M., 1993, Weathering and global denudation: *Journal of Geology*, v. 101, p. 295–303.
- MCLENNAN, S.M., HEMMING, S., MCDANIEL, D.K., AND HANSON, G.N., 1993, Geochemical approaches to sedimentation, provenance, and tectonics, in Johnsson, M.J., and Basu, A., eds., *Processes Controlling the Composition of Clastic Sediments*: Geological Society of America, Special Paper 284, p. 21–40.
- NESBITT, H.W., AND YOUNG, G.M., 1984, Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations: *Geochimica et Cosmochimica Acta*, v. 48, p. 1523–1534.
- NESBITT, H.W., AND YOUNG, G.M., 1989, Formation and diagenesis of weathering profiles: *Journal of Geology*, v. 97, p. 128–147.
- NESBITT, H.W., MARKOVICS, G., AND PRICE, R.C., 1980, Chemical processing affecting alkalis and alkaline earths during continental weathering: *Geochimica et Cosmochimica Acta*, v. 44, p. 1659–1666.
- NESBITT, H.W., AND MARKOVICS, G., 1997, Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments: *Geochimica et Cosmochimica Acta*, v. 61, p. 1653–1670.
- NESBITT, H.W., AND YOUNG, G.M., 1996, Petrogenesis of sediments in the absence of chemical weathering: effects of abrasion and sorting on bulk composition and mineralogy: *Sedimentology*, v. 43, p. 341–358.
- NESBITT, H.W., FEDO, C.M., AND YOUNG, G.M., 1997, Quartz and feldspar stability, steady and non-steady state weathering, and petrogenesis of siliciclastic sands and muds: *Journal of Geology*, v. 105, p. 173–191.
- NESBITT, H.W., YOUNG, G.M., MCLENNAN, S.M., AND KEAYS, R.R., 1996, Effects of chemical weathering and sorting of the petrogenesis of siliciclastic sediments, with implications for provenance studies: *Journal of Geology*, v. 104, p. 525–542.
- NETTLETON, W.D., FLACH, K.W., AND NELSON, R.E., 1970, Pedogenic weathering of tonalite in southern California: *Geoderma*, v. 4, p. 387–402.
- REUSS, J.O., AND JOHNSON, D.W., 1985, *Acid Deposition and the Acidification of Soils and Waters*: New York, Springer-Verlag, Ecological Studies 59, 119 p.
- TAYLOR, S.R., AND MCLENNAN, S.M., 1985, *The Continental Crust: Its Composition and Evolution*: Oxford, U.K., Blackwell Scientific Publications, 312 p.
- TREWARTHA, G.T., AND HORN, B.H., 1980, *An Introduction to Climate*: New York, McGraw-Hill, 416 p.
- WALAWENDER, M.J., GASTIL, R.G., CLINKENBEARD, J.P., MCCORMICK, W.V., EASTMAN, B.G., WERNICKLE, R.S., WARDLAW, M.S., BUN, S.H., AND SMITH, B.M., 1990, Origin and evolution of the zoned La Posta-type plutons, eastern Peninsular Ranges batholith, southern and Baja California, in Anderson, J.L., ed., *The Nature and Origin of Cordilleran Magmatism*: Geological Society of America, Memoir 174, p. 1–18.
- WARREN, H.N., AND GIRTY, G.H., 1999, A *Matlab* 5 program for calculating the statistics of mass change: *Journal of Geoscience Education*, v. 47, p. 313–320.
- WORONOW, A., AND LOVE, K.M., 1990, Quantifying and testing differences among means of compositional data suites: *Mathematical Geology*, v. 22, p. 837–852.
- YOUNG, G.M., AND NESBITT, H.W., 1998, Processes controlling the distribution of Ti and Al in weathering profiles, siliciclastic sediments, and sedimentary rocks: *Journal of Sedimentary Research*, v. 68, p. 448–455.

Received 29 December 2001; accepted 18 September 2002.