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CRYSTAL CHEMICAL DIFFERENCES IN Al-RICH SMECTITES AS SHOWN BY MULTIVARIATE ANALYSIS OF VARIANCE AND DISCRIMINANT ANALYSIS

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Abstract—Multivariate analysis of variance and discriminant analysis were used to establish the crystal chemistry of several Al-rich smectites. The statistical analyses were carried out on 78 samples taken from the literature which were classified on the basis of their physicochemical properties. A strong discrimination exists between beidellites and montmorillonites, 'non-ideal' montmorillonites and 'ideal' montmorillonites, and Wyoming-type and Cheto-type montmorillonites. Of the Cheto-type montmorillonites, the Tatatilla-type samples are strongly discriminated, whereas the distinction between Chambers- and Otay-types is not strong. Al^{IV}, Al^{VI}, Fe, Mg, and Ca are generally important discriminating variables, whereas the tetrahedral portion of the layer charge, commonly used as a discriminating factor among these minerals, is only moderately significant.

Key Words—Aluminum smectite, Beidellite, Chemical composition, Classification, Crystal chemistry, Discriminant analysis, Multivariate analysis.

INTRODUCTION

It has long been known that many of the physicochemical properties of smectites, e.g., cation-exchange capacity and thermal behavior, differ widely from sample to sample and that this behavior appears to be a function of the chemical composition of the samples. It therefore seems advisable to classify in a statistical manner various crystal chemical types of smectites on the basis of such physicochemical properties.

Historically, smectites have been divided into di- (Al-rich) and trioctahedral (Mg-rich) groups, of which the Al-rich, dioctahedral types will be treated here. Dioctahedral smectites have been further divided into montmorillonites and beidellites (see, e.g., Weir and Greene-Kelly, 1962), wherein beidellites represent the Al-rich members of a montmorillonite-beidellite series in which the net negative layer charge arises chiefly from tetrahedral substitutions rather than from octahedral substitutions. Conversely, in montmorillonites the net layer charge from octahedral substitutions is greater than or equal to that from tetrahedral substitutions. Montmorillonites and beidellites can be distinguished by a variety of tests, the most common being the lithium expansion test proposed by Greene-Kelly (1953) and improved upon by Byström Brusewitz (1976).

Grim and Kulbicki (1961) subdivided montmorillonites into Cheto-type and Wyoming-type materials on the basis of differences in cation-exchange capacity, thermal behavior after K and Mg treatments, and infrared absorption properties. These types also differ crystal chemically in that more Mg appears to be present in the octahedral layer of the Cheto-type than the Wyoming-type and that the cations in octahedral coordination are regularly distributed in the former and randomly distributed in the latter. Schomburg (1976) distinguished these two types on the basis of their dilatometric curves, and Landgraf (1979a, 1979b) reported differences in the relative intensity of the 001 X-ray diffraction reflections and in the optical properties of Cheto-type and Wyoming-type montmorillonites that had been treated with organic liquids.

Shultz (1969) retained the term Wyoming-type after Grim and Kulbicki (1961), but subdivided the Cheto-type into Otay,- Tatatilla-, and Chambers-types on the basis of differences in their differential thermal analysis (DTA) curves, the nature of their fired products, and their degree of re-expansion with ethylene glycol after K-saturation and heating to 300°C. Schultz (1969) also introduced the term "non-ideal" for those samples that showed a dehydroxylation DTA peak between 550° and 600°C, instead of a normal temperature of about 700°C, and which possessed less than an ideal 4 OH per unit cell. Brigatti and Poppi (1981) presented a mathematical model for distinguishing dioctahedral smectites using three variables which are functions of the chemical data. They examined literature analyses and included in their study materials classified on the basis of physicochemical properties as well as materials classified on the basis of chemical data alone. The usefulness of their statistical classification was limited due to the non-homogeneity of the literature data.

The aim of the present investigation was to extend the work of Brigatti and Poppi (1981) by (1) comparing the subdivision of Al-rich, dioctahedral smectites based on previously determined physical properties and

Table 1. Chemical formulae of smectites recalculated on the basis of $O_{10}(OH)_2$.

Sample number	Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω^1	Analysis number[2]	Reference
						Wyoming-type						
1	0.162	1.524	0.210	0.263	0.000	0.004	0.010	0.398	0.002	0.389	1	Schultz (1969)
2	0.101	1.548	0.172	0.338	0.000	0.005	0.008	0.213	0.030	0.409	2	Schultz (1969)
3	0.156	1.556	0.206	0.235	0.000	0.004	0.016	0.352	0.003	0.407	3	Schultz (1969)
4	0.094	1.562	0.175	0.283	0.000	0.006	0.019	0.233	0.028	0.326	4	Schultz (1969)
5	0.069	1.565	0.161	0.324	0.000	0.006	0.017	0.175	0.025	0.315	5	Schultz (1969)
6	0.179	1.541	0.278	0.182	0.000	0.009	0.000	0.316	0.011	0.554	6	Schultz (1969)
7	0.136	1.431	0.281	0.233	0.004	0.037	0.002	0.319	0.055	0.362	7	Schultz (1969)
8	0.188	1.369	0.348	0.321	0.000	0.028	0.100	0.022	0.084	0.664	8	Schultz (1969)
9	0.137	1.520	0.190	0.252	0.000	0.007	0.005	0.520	0.004	0.288	10	Schultz (1969)
11	0.197	1.580	0.200	0.240	0.000	0.010	0.041	0.241	0.018	0.584	13	Schultz (1969)
12	0.047	1.527	0.180	0.324	0.000	0.008	0.122	0.000	0.007	0.191	14	Schultz (1969)
13	0.154	1.567	0.200	0.250	0.000	0.000	0.000	0.362	0.003	0.438	15	Schultz (1969)
14	0.065	1.479	0.223	0.245	0.004	0.011	0.109	0.204	0.048	0.156	18	Schultz (1969)
15	0.122	1.641	0.091	0.272	0.001	0.023	0.140	0.027	0.000	0.425	20	Schultz (1969)
8G	0.000	1.791	0.088	0.148	0.000	0.000	0.000	0.048	0.000	0.000	8	Grim and Kulbicki (1961)
9G	0.089	1.653	0.194	0.087	0.000	0.000	0.046	0.088	0.212	0.239	9	Grim and Kulbicki (1961)
10G	0.058	1.694	0.179	0.184	0.000	0.000	0.021	0.049	0.002	0.830	10	Grim and Kulbicki (1961)
11G	0.035	1.620	0.245	0.189	0.000	0.000	0.039	0.001	0.010	0.571	11	Grim and Kulbicki (1961)
12G	0.202	1.619	0.285	0.199	0.000	0.000	0.000	0.099	0.018	2.171	12	Grim and Kulbicki (1961)
13G	0.157	1.623	0.302	0.139	0.000	0.016	0.009	0.011	0.015	3.857	13	Grim and Kulbicki (1961)
14G	0.122	1.614	0.293	0.137	0.000	0.018	0.012	0.016	0.017	2.307	14	Grim and Kulbicki (1961)
15G	0.134	1.538	0.326	0.207	0.000	0.016	0.024	0.011	0.009	2.093	15	Grim and Kulbicki (1961)
16G	0.286	1.754	0.193	0.189	0.000	0.000	0.000	0.076	0.015	4.290	16	Grim and Kulbicki (1961)
						Tatatilla-type						
18	0.102	1.572	0.003	0.424	0.004	0.000	0.263	0.000	0.000	0.197	28	Schultz (1969)
19	0.130	1.615	0.016	0.409	0.001	0.000	0.213	0.009	0.000	0.312	29	Schultz (1969)
20	0.260	1.660	0.047	0.356	0.000	0.000	0.184	0.009	0.055	0.607	30	Schultz (1969)
21	0.248	1.692	0.013	0.312	0.000	0.003	0.244	0.011	0.000	0.501	31	Schultz (1969)
22	0.256	1.773	0.025	0.242	0.000	0.000	0.159	0.067	0.000	0.672	32	Schultz (1969)
6G	0.099	1.576	0.003	0.425	0.000	0.000	0.257	0.000	0.000	0.194	6	Grim and Kulbicki (1961)
						Otay-type						
24	0.026	1.344	0.057	0.686	0.001	0.007	0.005	0.416	0.002	0.061	34	Schultz (1969)
25	0.111	1.344	0.050	0.752	0.000	0.000	0.103	0.179	0.044	0.261	35	Schultz (1969)
26	0.032	1.369	0.090	0.576	0.011	0.013	0.190	0.045	0.012	0.075	36	Schultz (1969)
27	0.046	1.390	0.098	0.534	0.000	0.016	0.007	0.430	0.024	0.101	37	Schultz (1969)
28	0.037	1.385	0.087	0.565	0.000	0.005	0.240	0.000	0.000	0.078	38	Schultz (1969)
29	0.086	1.412	0.096	0.533	0.001	0.019	0.186	0.025	0.046	0.203	39	Schultz (1969)
30	0.077	1.396	0.142	0.503	0.000	0.016	0.174	0.025	0.037	0.197	40	Schultz (1969)
31	0.020	1.471	0.053	0.451	0.002	0.007	0.003	0.500	0.012	0.039	41	Schultz (1969)
32	0.009	1.452	0.065	0.519	0.003	0.004	0.189	0.020	0.010	0.024	42	Schultz (1969)
33	0.049	1.454	0.127	0.459	0.000	0.051	0.055	0.037	0.041	0.268	44	Schultz (1969)
34	0.009	1.547	0.039	0.361	0.001	0.035	0.189	0.011	0.001	0.024	45	Schultz (1969)
2G	0.046	1.529	0.109	0.540	0.000	0.000	0.000	0.080	0.000	0.901	2	Grim and Kulbicki (1961)
						Chambers-type						
35	0.123	1.399	0.175	0.427	0.002	0.018	0.010	0.455	0.003	0.260	46	Schultz (1969)
36	0.111	1.468	0.144	0.401	0.003	0.014	0.193	0.021	0.028	0.269	47	Schultz (1969)
37	0.222	1.375	0.242	0.391	0.002	0.028	0.045	0.382	0.006	0.467	48	Schultz (1969)
38	0.008	1.434	0.088	0.469	0.000	0.015	0.007	0.423	0.006	0.018	49	Schultz (1969)
39	0.160	1.531	0.225	0.316	0.000	0.007	0.107	0.019	0.027	0.685	50	Schultz (1969)
40	0.076	1.317	0.147	0.525	0.000	0.010	0.055	0.421	0.074	0.128	51	Schultz (1969)
41	0.087	1.427	0.134	0.529	0.001	0.010	0.042	0.191	0.041	0.288	52	Schultz (1969)
42	0.125	1.357	0.266	0.461	0.001	0.031	0.111	0.043	0.011	0.595	55	Schultz (1969)
43	0.021	1.645	0.087	0.335	0.001	0.027	0.008	0.013	0.020	0.462	60	Schultz (1969)
1G	0.041	1.459	0.094	0.531	0.000	0.012	0.130	0.009	0.007	0.149	1	Grim and Kulbicki (1961)
						Non-ideal montmorillonite						
120	0.250	1.435	0.346	0.308	0.003	0.005	0.104	0.049	0.011	0.945	12	Brigatti (1983)
121	0.178	1.352	0.307	0.445	0.002	0.003	0.120	0.018	0.042	0.602	13	Brigatti (1983)

Table 1. Continued.

Sample number	Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω[1]	Analysis number[2]	Reference
45	0.138	1.088	0.627	0.240	0.000	0.021	0.008	0.455	0.015	0.323	64	Schultz (1969)
46	0.173	1.328	0.293	0.454	0.001	0.034	0.078	0.086	0.037	0.647	65	Schultz (1969)
47	0.170	1.357	0.274	0.313	0.000	0.054	0.009	0.408	0.025	0.391	66	Schultz (1969)
48	0.118	1.358	0.312	0.449	0.000	0.024	0.059	0.000	0.000	1.026	67	Schultz (1969)
49	0.074	1.256	0.383	0.391	0.000	0.000	0.000	0.388	0.003	0.198	68	Schultz (1969)
89	0.172	1.339	0.320	0.460	0.002	0.011	0.140	0.021	0.049	0.758	5	Poppi and Brigatti (1976)
90	0.156	1.123	0.589	0.359	0.006	0.008	0.170	0.039	0.029	0.610	6	Poppi and Brigatti (1976)
97	0.159	1.339	0.320	0.430	0.003	0.008	0.140	0.100	0.030	0.557	13	Poppi and Brigatti (1976)
117	0.163	1.115	0.566	0.350	0.002	0.005	0.167	0.038	0.027	0.411	9	Brigatti (1983)
118	0.449	0.866	0.531	0.817	0.005	0.002	0.263	0.026	0.055	0.745	10	Brigatti (1983)
119	0.589	1.397	0.461	0.392	0.005	0.003	0.077	0.028	0.028	2.845	11	Brigatti (1983)
						Beidellite						
50	0.513	1.990	0.022	0.009	0.000	0.000	0.001	0.454	0.008	1.116	69	Schultz (1969)
52	0.416	1.395	0.495	0.079	0.000	0.000	0.223	0.143	0.000	0.710	71	Schultz (1969)
53	0.439	1.443	0.323	0.262	0.003	0.031	0.175	0.087	0.066	0.898	73	Schultz (1969)
54	0.385	1.285	0.334	0.376	0.000	0.030	0.082	0.371	0.126	0.585	74	Schultz (1969)
55	0.314	1.350	0.444	0.142	0.000	0.033	0.121	0.040	0.253	0.613	75	Schultz (1969)
51	0.541	1.964	0.046	0.018	0.000	0.000	0.226	0.015	0.012	1.140	70	Schultz (1969)
56	0.364	1.833	0.020	0.197	0.000	0.013	0.156	0.011	0.040	1.014	76	Schultz (1969)
57	0.703	2.022	0.026	0.000	0.000	0.000	0.021	0.510	0.009	1.263	77	Schultz (1969)
58	0.496	1.902	0.147	0.154	0.001	0.000	0.000	0.029	0.034	9.990	78	Schultz (1969)
59	0.670	2.001	0.000	0.000	0.000	0.000	0.000	0.670	0.000	1.005	79	Schultz (1969)
60	0.329	2.001	0.000	0.000	0.000	0.000	0.000	0.330	0.000	1.012	80	Schultz (1969)
						Cheto-type						
3G	0.000	1.384	0.095	0.700	0.000	0.013	0.016	0.020	0.013	0.000	3	Grim and Kulbicki (1961)
4G	0.044	1.505	0.118	0.580	0.000	0.000	0.000	0.037	0.000	3.277	4	Grim and Kulbicki (1961)
5G	0.100	1.464	0.119	0.653	0.000	0.000	0.021	0.029	0.000	2.128	5	Grim and Kulbicki (1961)

[1] Tetrahedral portion of layer charge.
[2] Sample number used in quoted references from which values were recalculated.

physicochemical tests only and the subdivision based on the chemistry of the samples; (2) defining the chemical variables which are most significant in this subdivision; and (3) providing discriminant functions which describe the differences of the group within a simple model that maximizes these differences and yields classification functions that are able to place a sample into its correct type solely from its chemical composition. To this end, multivariate factor analysis and discriminant analysis were used.

CHOICE OF DATA

This work used chemical analyses of samples that other authors had classified into the different types of Al-rich smectites according to their physicochemical properties only (for example Li- and/or K-tests, heating behavior; Grim and Kulbicki, 1961; Schultz, 1969) or that we have classified on the basis of similar tests provided by the authors. Chemical analyses were used only when the impurities were found to be no greater than 10% and due to no more than two phases with well-defined chemical compositions. Such analyses were subsequently adjusted for impurities. Grim and Kulbicki (1961) did not subdivide their Cheto-type montmorillonites into Otay-, Chambers-, and Tatatilla-types. In the part of the present study that required this subdivision, only the analyses of those samples found in the same localities studied and classified by Schultz (1969) were considered.

Analyses with an $Fe_2O_3 + FeO > 11\%$ were eliminated because above this value the *b* cell parameter varies as a function of Fe content, as in nontronites (Russell and Clark, 1978; Brigatti, 1983). Formulae whose octahedral cation contents were greater than 2.26 on the basis of $O_{10}(OH)_2$ were rejected even if the *b* cell parameter showed that the sample was dioctahedral. In our data, in fact, a gap between 2.26 and 2.40 was found. Schultz's sample 27 was ignored in the discriminant analysis because it was defined by him as an intermediate between the Wyoming- and Chambers-type.

The iron in all analyses was considered as Fe^{3+} inasmuch as many authors reported total iron as Fe^{3+} only and because Fe^{3+} and Fe^{2+} are both found in smectites in octahedral sites, normally with $Fe^{3+} >> Fe^{2+}$ (Rozenson and Heller-Kallai, 1977).

The weight percentage of adsorbed H_2O in montmorillonites is a function of environmental parameters that are difficult to standardize (relative humidity, temperature at the time of analysis, etc., Prost, 1976; Del Pennino *et al.*, 1981). In addition, the H_2O percentage was not reported for many materials as the analysis was carried out on ignited samples. For this reason water was not considered in the statistical analysis even if it may be an important discriminating element. Finally, structural formulae were rejected if the unbalance between the layer charges and the interlayer charges was >0.05 and Si >4, on the basis of $O_{10}(OH)_2$.

Structural formulae were used in the statistical analysis; the literature sources of the chemical analyses from which the formulae were recalculated are listed in Table 1. The formulae were recalculated by: (1) balancing the cation charges on the basis of 22 negative charges $O_{10}(OH)_2$; (2) assigning all Si to the tetrahedral layer together with enough Al to bring the total to 4; (3) assigning only Ca, Na, and K to interlayer positions; and (4) assigning all other cations to the octahedral layer.

According to many authors, Mg and Al can also be present as exchangeable cations because these cations are common in the exchange liquid. Mg and Al were not assigned to exchangeable positions because of the following: (1) As stated by Fripiat *et al.* (1971), octahedral cations may enter in the exchange liquid because of octahedral hydrolysis during the process. Also, Novák and Čičel (1978) showed a remarkable dependence of the apparent dissolution rate of the octahedral layer of smectite on the degree of substitution of Fe^{2+} and Mg^{2+} for Al^{3+} in octahedral positions. Thus, cation distributions in smectites may be far from the ideal net dioctahedral occupancy in the montmorillonite-beidellite series. (2) No crystal chemical evidence exists that favors a strictly dioctahedral smectite over a smectite with an octahedral occupancy greater than 2.0. (3) The amount of Al and Mg in interlayer positions is normally low. (4) For a considerable number of analyses used in this work, Mg and Al were not determined in the exchanged liquid.

An attempt was also made to verify whether the statistical analysis was in agreement or not with these selection criteria. A discriminant analysis and a multivariate analysis of variance were carried out to this end both on the structural formulae re-calculated by us and on those calculated by Schultz (1969) using the Ross and Hendricks (1945) method. Using the Wyoming-type and Cheto-type subdivision as a check and the subdivision that comprises all species and/or types, the results show comparable significance in discrimination of sample groups.

Table 2 summarizes the subdivision of the Al-rich smectites adopted in the present study. The 'ideal' and 'non-ideal' (Schultz, 1969) subdivisions of beidellites is not considered here inasmuch as Schultz found all

Table 2. Subdivision of Al-rich smectites used in the statistical analysis.

Subgroup	Species	Type	Type	Type
Al-rich smectites	beidellite (Weir and Greene-Kelly, 1962)			
	montmorillonite	'non-ideal' montmorillonite (Schultz, 1969)		
		'ideal' montmorillonite	Wyoming (Grim and Kulbicki, 1961)	
			Cheto (Grim and Kulbicki, 1961)	Otay (Schultz, 1969) Chambers (Schultz, 1969) Tatatilla (Schultz, 1969)

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Table 3. Minimum, maximum, mean, and standard deviations for cation concentration and Ω.[1]

Smectite type	No. of samples		Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω
Otay	12	x_{min}	0.009	1.344	0.039	0.361	0.000	0.000	0.000	0.000	0.000	0.024
		x_{max}	0.111	1.547	0.142	0.752	0.011	0.051	0.240	0.500	0.046	0.901
		$\bar{x}$	0.046	1.424	0.084	0.540	0.002	0.014	0.112	0.147	0.019	0.186
		σ_x	0.031	0.067	0.032	0.103	0.003	0.015	0.092	0.189	0.018	0.242
Tatatilla	6	x_{min}	0.099	1.572	0.003	0.242	0.000	0.000	0.159	0.000	0.000	0.194
		x_{max}	0.260	1.773	0.047	0.425	0.004	0.003	0.263	0.067	0.055	0.672
		$\bar{x}$	0.183	1.648	0.018	0.361	0.001	0.001	0.220	0.016	0.009	0.414
		σ_x	0.080	0.077	0.166	0.073	0.002	0.001	0.042	0.025	0.022	0.208
Chambers	10	x_{min}	0.008	1.317	0.087	0.316	0.000	0.007	0.007	0.009	0.003	0.018
		x_{max}	0.222	1.645	0.266	0.531	0.003	0.031	0.193	0.455	0.074	0.685
		$\bar{x}$	0.097	1.441	0.160	0.439	0.001	0.017	0.071	0.198	0.022	0.332
		σ_x	0.066	0.094	0.065	0.078	0.001	0.009	0.062	0.199	0.022	0.214
Cheto (Otay + Tatatilla + Chambers)	31	x_{min}	0.000	1.317	0.003	0.242	0.000	0.000	0.000	0.000	0.000	0.000
		x_{max}	0.260	1.773	0.266	0.752	0.011	0.051	0.263	0.500	0.074	3.277
		$\bar{x}$	0.089	1.476	0.099	0.483	0.001	0.012	0.110	0.127	0.017	0.434
		σ_x	0.075	0.114	0.066	0.120	0.002	0.012	0.092	0.174	0.020	0.665
Wyoming	23	x_{min}	0.000	1.369	0.088	0.087	0.000	0.000	0.000	0.000	0.000	0.000
		x_{max}	0.286	1.791	0.348	0.338	0.004	0.037	0.140	0.520	0.212	4.290
		$\bar{x}$	0.126	1.579	0.218	0.228	0.000	0.009	0.032	0.164	0.027	0.951
		σ_x	0.065	0.094	0.067	0.067	0.001	0.010	0.043	0.154	0.045	1.176
'Ideal' montmorillonite (Wyoming + Cheto)	54	x_{min}	0.000	1.317	0.003	0.087	0.000	0.000	0.000	0.000	0.000	0.000
		x_{max}	0.286	1.791	0.348	0.752	0.011	0.051	0.263	0.520	0.212	4.290
		$\bar{x}$	0.105	1.520	0.150	0.374	0.001	0.011	0.077	0.143	0.021	0.654
		σ_x	0.072	0.117	0.089	0.162	0.002	0.011	0.084	0.166	0.033	0.944
'Non-ideal' montmorillonite	13	x_{min}	0.074	0.866	0.274	0.240	0.000	0.000	0.000	0.000	0.000	0.198
		x_{max}	0.589	1.435	0.627	0.817	0.006	0.054	0.263	0.455	0.055	2.845
		$\bar{x}$	0.215	1.258	0.410	0.416	0.002	0.014	0.103	0.127	0.027	0.774
		σ_x	0.144	0.163	0.127	0.138	0.002	0.016	0.076	0.168	0.017	0.666
'Ideal' + 'non-ideal' montmorillonite	67	x_{min}	0.000	0.866	0.003	0.087	0.000	0.000	0.000	0.000	0.000	0.000
		x_{max}	0.589	1.791	0.627	0.817	0.011	0.054	0.263	0.520	0.212	4.290
		$\bar{x}$	0.126	1.469	0.200	0.382	0.001	0.011	0.082	0.140	0.022	0.677
		σ_x	0.099	0.163	0.142	0.157	0.002	0.012	0.083	0.165	0.031	0.893
Beidellite	11	x_{min}	0.314	1.285	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.585
		x_{max}	0.703	2.022	0.495	0.376	0.003	0.033	0.226	0.670	0.253	9.990
		$\bar{x}$	0.470	1.744	0.169	0.112	0.000	0.010	0.091	0.242	0.050	1.759
		σ_x	0.130	0.305	0.192	0.127	0.001	0.014	0.093	0.234	0.077	2.739
Whole population	78	x_{min}	0.000	0.866	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		x_{max}	0.703	2.022	0.627	0.817	0.011	0.054	0.263	0.670	0.253	9.990
		$\bar{x}$	0.174	1.508	0.196	0.344	0.001	0.011	0.083	0.154	0.026	0.830
		σ_x	0.159	0.210	0.149	0.180	0.002	0.013	0.084	0.178	0.041	1.342

[1] Ω = tetrahedral portion of the layer charge.

natural beidellites to have a 'non-ideal' behavior. The variables used in the statistical analysis were Al^{IV}, Al^{VI}, Fe, Mg, Mn, Ti, Ca, Na, K, and Ω, where Ω is the tetrahedral portion of the layer charge. This ratio is >1.0 when the octahedral charge is >6.0 on the basis of $O_{10}(OH)_2$. In the statistical analysis 9.99 was arbitrarily assumed to be the maximum value of Ω. Table 3 contains the minimum, maximum, and mean values, and the standard deviation for the variables used of all types.

DESCRIPTION OF THE METHODS

The problem was to discriminate a collection of n samples of Al-rich smectites, for each one of which m chemical elements had been determined, between g different groups on the basis of chemical analyses. The groups were obtained with an *a priori* criterion, i.e., by means of their physicochemical behavior only. The samples can be considered to be distributed in a m-dimensional space, in more or less g-elliptical clouds

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Table 4. Parameters derived for the canonical discriminant functions.

Analysis[1]	Function[2]	Wilks' Λ[2]	Approx. F[2]	Significance
1	1	0.3165	25.552	0.0000
2	1	0.1062	19.229	0.0000
3	1	0.3705	35.677	0.0000
4	1	0.2278	32.545	0.0000
5	1 to 2	0.0473	9.764	0.0000
	2	0.4553	3.889	0.0082
6	1	0.3481	4.681	0.0064
7	1 to 5	0.0232	9.365	0.0000
	2 to 5	0.1240	6.315	0.0000
	3 to 5	0.4090	3.679	0.0000
	4 to 5	0.7727	1.748	0.0684
	5	0.9930	0.113	0.9761

[1] See text for samples included in analysis.
[2] See text.

of points whose center of gravity is designated a centroid.

If g is equal to 2, an optimum way to separate the two clouds is by means of a line whose perpendicular is called a discriminant function. The projection of all of the specimens onto this line should show that most of those in group 1 fall to the left of a central point, and that most of those in group 2 fall to the right of the point. The first objective was to verify whether the "null hypothesis," that is, whether the group cannot be discriminated, can be rejected. Such a discrimination is normally estimated by the Wilks test named "Wilks' Λ criterion" (Wilks, 1932). A low Wilks' Λ value indicates a good discrimination, i.e., most specimens fall on the same side of the central point of a separation line (for example on the left) if they belong to group 1, or fall on the other side of the central point if they belong to group 2. The Wilks' Λ value, an approximate F test for Λ (SPSS-X Statistical Algorithms, 1983) and the significance of the "null hypothesis" for the present discriminant analyses are shown in Tables 4 and 9, whereas the significance for all the variables individually for the same analysis is listed in Tables 5 and 10.

The discriminant function can be expressed as an equation of the form:

$$Z_n = b_i X_{in},$$

where Z_n is the discriminant score, i.e., the projection of the nth specimen onto the line, b_i is the weight to be obtained by the statistical method of discriminant analysis, and X_{in} is the number of the atoms of each chemical element *per unit cell.*

The method can be extended to more than two groups of samples; here $(g - 1)$ discriminant functions are required. Every function has a different discriminating power, and under certain circumstances the number of functions can be less than $(g - 1)$ without a considerable loss of discriminating power. Together with the b_i coefficients, coefficients of the canonical discriminant functions can be obtained. These coefficients give, when the sign is ignored, the contribution of their associated variables to the discriminant functions (Tables 6 and 10), whereas the discriminant functions give the best separation among the groups. Classification or Fisher's functions give for each specimen, which may or may not be part of the original set, the group to which it most likely belongs (Tables 7 and 10).

The form of the classification functions (Fisher's linear discriminant functions) is:

$$C_k = c_{k0} + \sum_{j=1}^{m} c_{kj} Y_{jn},$$

where C_k is the classification score for the group k, Y_{jn} is the value of the jth chemical element of the nth sample to be classified, c_{kj} are the classification coefficients, and c_{k0} is a constant. The Y_n vector variable will be one of the X_n-dependent vector variables if the sample has been used in the discrimination process: it will not be one of the X_n-dependent vector variables if the sample is used only in the classification process. For every sample, knowing its chemical formula on the basis of 22 negative charges $O_{10}(OH)_2$ and the c_{kj} coefficients, the classification functions give g classification scores C_k, one for each of the g groups consid-

Table 5. Significances of the "null hypothesis" for the chemical variables on analyses 1–7.[1]

Analysis[1]	Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω[2]
1	0.000	0.000	0.522	0.000	0.237	0.729	0.727	0.078	0.037	0.012
2	0.000	0.000	0.001	0.000	0.012	0.530	0.745	0.178	0.310	0.221
3	0.000	0.000	0.000	0.394	0.015	0.409	0.313	0.766	0.532	0.667
4	0.065	0.001	0.000	0.000	0.158	0.411	0.000	0.413	0.276	0.045
5	0.000	0.000	0.000	0.001	0.754	0.022	0.002	0.144	0.465	0.117
6	0.025	0.631	0.002	0.019	0.579	0.611	0.247	0.550	0.712	0.154
7	0.000	0.000	0.000	0.000	0.053	0.118	0.000	0.215	0.424	0.059

[1] See text for samples included in analysis.
[2] Ω as in Table 3.

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ered. The sample is attributed to a group on the basis of the highest score.

The probability of group membership P_k (posterior probability) can be calculated from

$$P_k = \exp(C_k) / \sum_{k=1}^{g} \exp(C_k).$$

A statistical package for the social sciences (SPSS) (subprograms MANOVA and DISCRIMINANT) was used in this research (Nie *et al.*, 1975). In the discriminant analysis, independent variables were selected on the basis of their discriminant power using an upward stepwise method. This method was preferred to one that uses all p independent variables because generally a number of discriminating variables $p' < p$ achieves an equally satisfactory discrimination. The discrimination criterion selected is the "Mahalanobis" distance which seeks to maximize the distance between the two closest groups (Mahalanobis, 1936).

A detailed discussion on multivariate factor analysis can be found in Morrison (1978) and in Cooley and Lohnes (1971).

RESULTS

Analysis (1). Montmorillonite and beidellite

To define types or species of Al-rich smectites, the two end members, montmorillonites and beidellites were compared. The discrimination between the two species is significant as shown by the Wilks Λ values reported in Table 4. Al^{IV}, Al^{VI}, and Mg, are highly significant elements; Ω is a significant variable, as well (Table 5). The canonical variables listed in Table 6 indicate that Al^{IV}, Al^{VI}, and, to a lesser amount, K and Na are the discriminant variables of greatest significance for discrimination.

According to Weir and Greene-Kelly (1962), the term beidellite should be used for the Al-rich members of montmorillonite-beidellite series with charge of the tetrahedral sheet greater than or equal to the charge of the octahedral sheet. Our results confirm the great importance of the Al content in both the octahedral and in tetrahedral sheets in discrimination and classification. For this and subsequent analyses, Fisher's classification-function coefficients for the two species are reported in Table 7. Only one of the 78 samples, a 'non-ideal' montmorillonite, was classified incorrectly as shown in Figure 1.

Schultz (1969) showed that the dehydroxylation temperature of natural beidellites is ~550°–600°C, a temperature range that is more or less characteristic of 'non-ideal' montmorillonites; this similar thermal behavior, together with the fact that the only incorrectly classified sample was a 'non-ideal' montmorillonite suggested the following comparison of these two groups of samples.

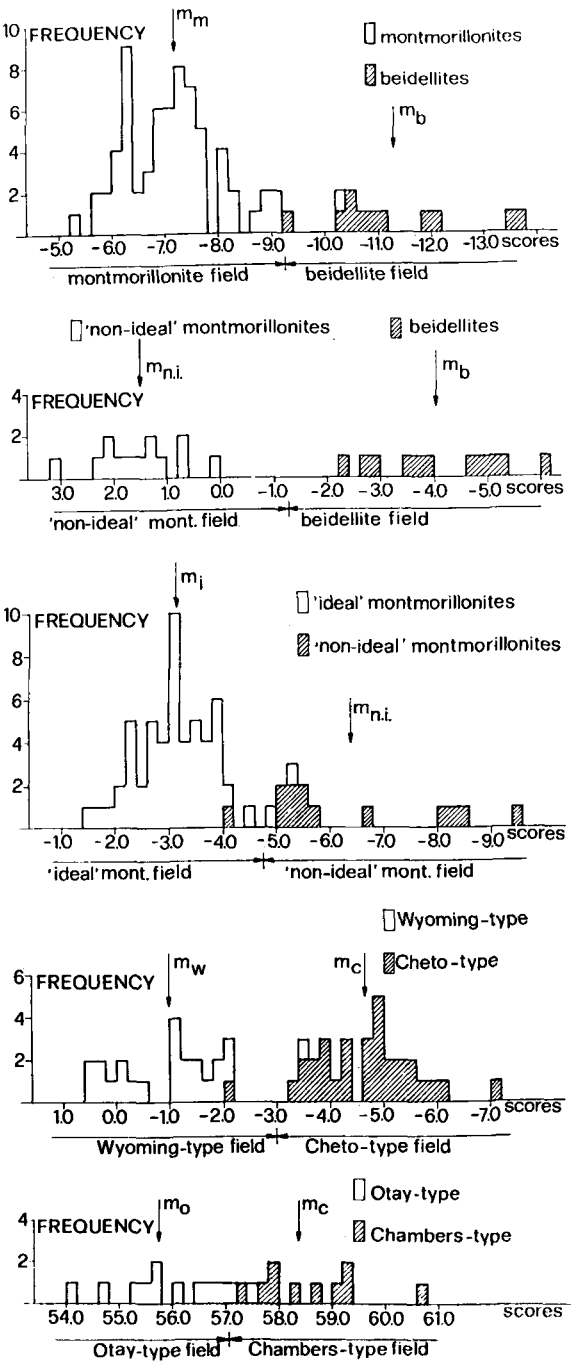

Figure 1. Histogram of the sample scores, as given by the unstandardized discriminant function, and their classification on the basis of Fisher's functions for the analyses: (1), (2), (3), (4), and (6) (see text). m represents the centroid for the reported species and/or types.

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Table 6. Unstandardized discriminant function coefficients and canonical variables.[1]

Analysis[2]		Function	Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω[3]
1	Unstandardized coefficients	1	−7.8296	−3.4956	*	*	*	−19.5200	−3.7596	−1.9918	−10.8632	*
	Canonical variables	1	−0.7950	−0.3510	*	*	*	0.0271	−0.0273	−0.1395	−0.1656	*
2	Unstandardized coefficients	1	*	*	5.5242	7.5324	203.7727	*	−23.8524	−6.9282	−20.4642	−0.5938
	Canonical variables	1	*	*	0.2702	0.4098	0.2014	*	0.0242	−0.1022	−0.0763	−0.0925
3	Unstandardized coefficients	1	*	*	−11.6002	−2.8949	*	*	−4.0395	*	*	*
	Canonical variables	1	*	*	−0.8246	−0.0817	*	*	−0.0967	*	*	*
4	Unstandardized coefficients	1	−4.9889	*	9.9678	−8.9355	*	−42.3157	−3.2865	*	*	*
	Canonical variables	1	0.1417	*	0.4910	−0.6913	*	−0.0624	−0.2825	*	*	*
5	Unstandardized coefficients	1	−5.5191	−0.9148	33.3924	*	*	−38.7548	−24.4867	−8.5681	*	−6.9629
		2	11.3970	16.4114	31.8016	*	*	−65.8176	−8.9849	−2.4694	*	−7.3807
	Canonical variables	1	−0.2446	−0.3773	0.3892	*	*	0.2025	−0.2672	0.1391	*	−0.0744
		2	0.5832	0.3734	0.4530	*	*	−0.0409	−0.0462	0.0254	*	0.3418
6	Unstandardized coefficients	1	*	32.7714	61.3342	13.7458	*	−44.3067	−7.9934	*	*	−9.4990
	Canonical variables	1	*	0.0797	0.5794	−0.4176	*	0.0844	−0.1948	*	*	0.2424
7	Unstandardized coefficients	1	−8.2523	4.4533	5.0524	10.9076	*	10.3285	−2.3751	*	−8.3372	−0.1044
		2	−2.0514	11.4958	21.3990	7.6739	*	7.0257	−7.5331	*	−3.3965	−0.3722
		3	7.2442	−1.5911	0.8999	4.5612	*	18.6116	3.8918	*	−5.4014	−0.0654
	Canonical variables	1	−0.6587	−0.3682	−0.0306	0.6391	*	0.0815	0.0222	*	−0.1078	−0.1842
		2	0.0111	−0.3342	0.7249	−0.1609	*	0.0781	−0.3116	*	0.0434	0.0681
		3	0.5787	−0.5498	0.3768	0.6372	*	0.1272	0.4856	*	0.0328	−0.0257

[1] The symbol * is used when the upward stepwise method does not include the element in the statistical analysis.
[2] See text for samples included in analysis.
[3] Ω as in Table 3.

Analysis (2). 'Non-ideal' montmorillonite and beidellite

'Non-ideal' montmorillonites and beidellites were strongly discriminated (Table 4; Figure 1) with Al^{VI}, Al^{IV}, Mg, and Fe being the best discriminating chemical variables (Table 5). In 'non-ideal' montmorillonites, Fe and Mg compensate for the shortage of Al^{VI}. Stepwise analysis shows that Mg and Fe are sufficient for a proper classification (Table 6). All samples examined were correctly classified (Figure 1).

Analysis (3). 'Ideal and 'non-ideal' montmorillonite

Statistical analyses showed that 'ideal' and 'non-ideal' montmorillonites that can be distinguished by their dehydroxylation temperature can also be differentiated by their chemical composition. Al^{IV}, Al^{VI}, and Fe are the best discriminating chemical variables (Table 5); the others are only very slightly significant. The significance of Mn, as in analysis (2), is doubtful. The only variables used for discrimination in stepwise analysis were Fe, Mg, and Ca, and of these, Fe was the most important (Table 6). Three of sixty-seven were misclassified, as is shown in Figure 1.

Analysis (4). Wyoming- and Cheto-type montmorillonite

For distinguishing between the Wyoming- and Cheto-type of montmorillonites, Al, Fe, Mg, and Ca were found to be the most important discriminant variables (Table 5). Mg, Fe, and Ca, in that order, contribute most to the discriminant function. Of the 54 samples examined, only two were misclassified (Figure 1).

Analysis (5). Otay-, Chambers-, and Tatatilla-type montmorillonite

Analysis (5) addressed the Cheto-type subdivision of Schultz (1969). Here, three types were compared, and, consequently, there were two discriminant functions. Only sample 30 (Table 1), an Otay-type montmorillonite, of 28 was misclassified into the Chambers-type field. Important variables in discrimination were found to be Al^{IV}, Al^{VI}, Fe, Mg, and Ca (Table 5). The most interesting result is the distinction between Tatatilla-type and the Chambers- and Otay-types (Figure 2). The Tatatilla-type is clearly well-defined, which had not been clarified previously. Function 1 in Table 6 gives the discrimination between the Tatatilla-type and the Otay- and Chambers-types. The most important variables were found to be Al^{VI}, Fe, and, to a lesser degree, Ca and Al^{IV}. Function 2 seems to be responsible for the Otay-type and Chambers-type subdivision.

Analysis (6). Chambers- and Otay-type montmorillonite

To clarify the discrimination of the Otay- and Chambers-type of montmorillonites, these two types only were considered in analysis (6). Table 5 shows that Fe is the most important discriminating variable; Mg and Al^{IV} were much less important. The low significance of all chemical variables, Fe excluded (Table 5), causes the relatively low significance of the discrimination between Otay- and Chambers-type montmorillonites (0.0064) (Table 4). Only one sample, the same as in Otay–Chambers–Tatatilla-type analysis is misclassified (Figure 1). In Schultz's (1969) analyses, Mg and Al were commonly found in interlayer sites. To verify whether this distribution was responsible for this low significance, discriminant analysis was made of 20 Otay- and Chambers-type montmorillonites taken from Schultz and using his formulae. The significant variables were found to be Fe^{3+}, Mg, Al^{IV}, and Ω (0.001, 0.022, 0.007, 0.004, respectively). In analysis (6) Ω was not significant (0.152 of Table 5). The significance of the discrimination is 0.0008, a relatively low value when compared with the significance of the other analyses, but better than the 0.0064 value of the analysis (6). Two samples are misclassified. The difference in the analysis significances is attributable to the differences in the significance of Ω which were strongly influenced by the two samples (2G and 1G of Table 1) of Grim and Kulbicki (1961). This result is surprising as those two samples are from Otay and Chambers localities, respectively. On the basis of these results, a definite crystal chemical characterization of the subdivision into Otay- and Chambers-type crystal chemistry, as proposed by Schultz (1969), may not be justified. Unfortunately the present study was carried out on only a few samples. More samples might clarify the problem.

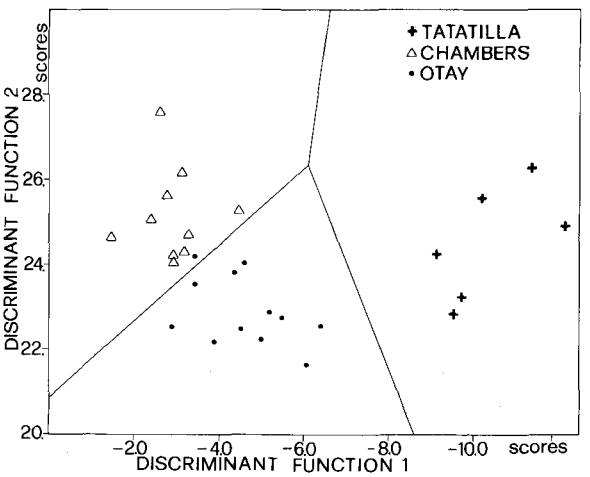

Figure 2. Plot of the sample scores in analysis (5) (see text).

Analysis (7). Whole population

Multivariate analysis of variance of all types of samples showed Al^{IV}, Al^{VI}, Mg, Fe, and Ca to be the most

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Table 7. Classification function coefficients (Fisher's linear discriminant functions).[1]

Analysis[2]	Species or type	Al^{IV}	Al^{VI}	Fe	Mg	Mn	Ti	Ca	Na	K	Ω[3]	Constant
1	montmorillonite	10.46	70.18	*	*	*	374.90	92.20	34.73	110.40	*	−62.41
	beidellite	43.09	84.75	*	*	*	456.25	107.87	43.03	155.68	*	−100.96
2	'non-ideal' montmorillonite	*	*	14.42	26.72	−179.51	*	29.23	21.87	−19.89	1.14	−12.07
	beidellite	*	*	−16.37	−15.26	−1315.19	*	162.17	60.48	94.17	4.45	−19.20
3	'ideal' montmorillonite	*	*	34.27	22.09	*	*	11.86	*	*	*	−7.84
	'non-ideal' montmorillonite	*	*	71.93	31.49	*	*	24.97	*	*	*	−23.27
4	Wyoming	29.56	*	56.04	36.42	*	−18.27	27.34	*	*	*	−13.17
	Cheto	47.79	*	19.62	69.07	*	136.35	39.35	*	*	*	−23.41
5	Otay	−192.35	645.03	821.22	*	*	−948.13	311.07	185.66	*	−89.69	−506.65
	Chambers	−175.87	680.54	948.96	*	*	−1161.63	249.76	165.72	*	−118.01	−554.58
	Tatatilla	−141.23	678.15	683.01	*	*	−836.80	436.75	230.78	*	−62.14	−589.92
6	Otay	*	6097.27	8252.62	3841.94	*	−1140.92	−481.63	*	*	−1423.48	−5561.20
	Chambers	*	6183.14	8413.34	3877.95	*	−1257.01	−502.58	*	*	−1448.37	−5711.31
7	Wyoming	−259.57	1693.98	1789.31	1301.72	*	2074.42	−18.28	*	164.51	−42.06	−1657.72
	Tatatilla	−245.58	1651.74	1716.29	1277.52	*	2027.79	29.17	*	162.11	−40.82	−1582.54
	Chambers	−259.24	1684.85	1771.13	1318.06	*	2147.25	−15.97	*	148.48	−41.98	−1646.71
	Otay	−264.59	1675.01	1751.12	1320.53	*	2129.40	−7.08	*	146.20	−41.50	−1631.60
	'non-ideal' montmorillonite	−250.63	1708.19	1823.19	1330.94	*	2130.01	−17.18	*	138.93	−42.78	−1698.84
	beidellite	−208.45	1653.48	1733.57	1254.09	*	2077.28	3.73	*	197.38	−41.15	−1590.64

[1] The symbol * is used when the upward stepwise method does not include the element in the statistical analysis.
[2] See text for samples used in analyses.
[3] Ω as in Table 3.

Table 8. Summary of the correctness of the classification for analysis (7) (whole population).

Species or type[1]	No. of samples	MOO	MOT	MOC	MOW	MON	MOB	% of samples correctly classified
MOO	12	10		2				83
MOT	6		6					100
MOC	10	3		6	1			60
MOW	23			2	20	1		87
MON	13					13		100
MOB	11						11	100

[1] MOO = Otay-type; MOT = Tatatilla-type; MOC = Chambers-type; MOW = Wyoming-type; MON = 'non-ideal' montmorillonite; MOB = beidellite.

Table 9. Parameters of the canonical discriminant functions for the five smectite classes.

Functions[1]	Wilks' Λ^1	Approx. F^1	Significance
1 to 4	0.0261	10.6924	0.0000
2 to 4	0.1367	7.4547	0.0000
3 to 4	0.4124	5.0147	0.0000
4	0.7767	3.0426	0.0095

[1] See text.

important variables (Table 5). The significance of other elements (e.g., Ω) was weak, or non-existent. Five discriminant functions were obtained, but three explain 96% of variance. The fourth function was not very significant, and the fifth was not significant (Table 4). Thus, only three functions were considered (discriminant function coefficients and canonical variables are listed in Table 6). Canonical variables showed that in discriminant function the weight of the elements is in order, for the first function—Al^{IV}, Mg, Al^{VI}; for the second function—Fe, Al^{VI}, Ca; for the third function—Mg, Al^{IV}, Al^{VI}, Ca. Table 7 reports the coefficients of Fisher's classification functions.

Table 8 reports a summary of samples correctly and incorrectly classified; nine of seventy-five samples were incorrectly classified: five of these were misclassified in the Otay- and Chambers-type field. This behavior is understandable if the low discrimination between the two groups, as previously shown, is considered.

DISCUSSION AND CONCLUSIONS

Tables 5 and 6 show that a classification and discrimination of Al-rich smectites can be made by considering cations in tetrahedral, octahedral, and interlayer sites. The very high degree of discrimination shown by Table 4 and by Figures 1 and 2 confirm the classifications of Grim and Kulbicki (1961), Weir and Greene-Kelly (1962), and Schultz (1969) based on physical properties or on chemical-physical test behavior. For the octahedral cations, the most significant elements were Al^{VI}, Mg, and Fe; Ti was not at all significant. Mn was weakly significant for some analyses, but this element was not analyzed in all samples, e.g., the Grim and Kulbicki (1961) samples. Only Ca was a significant discriminating element among interlayer cations. Al^{IV} was highly significant.

According to Schultz (1969) two chemical variables only allow a subdivision of Al-rich smectites to be made: the total net layer charge and the percentage of the total net layer charge in the tetrahedral sheets. The first variable differentiates the Wyoming-type montmorillonites from the remaining types and/or species; the second variable differentiates among the Otay-, Chambers-, and Tatatilla-types and beidellites.

Weir and Greene-Kelly (1962) emphasized that beidellite is an Al-rich end member of the montmorillonite-beidellite series; Al, in fact, is very high both in tetrahedral and octahedral sheets (Table 3), the amount of Fe is within the average for Al-rich smectites, and Mg is very low and has a very high significance (Table 5). Ω is very high in beidellites even if its significance was found to be much lower than was expected. The small amount of K in interlayer position makes this variable quite important. This result is not in agreement with the observations of Weir and Greene-Kelly (1962).

The dehydroxylation peak temperature of both natural beidellites and 'non-ideal' montmorillonites is 550°–600°C, which is much lower than for other montmorillonites. The difference in the chemical composition of these two species is marked both in the tetrahedral and the octahedral sheets, as shown in Table 3 and in Figure 1.

'Non-ideal' montmorillonites differ from 'ideal' montmorillonites in their distribution of Al in the tetrahedral and octahedral sites and their higher amount in Fe. According to Brigatti (1983) the dehydroxylation peak at 600°C is typical of smectites with an iron content in the range 0.60–0.25 atoms per half cell as in the 'non-ideal' montmorillonites examined here.

Grim and Kulbicki (1961) divided Al-smectites into Cheto- and Wyoming-types on the basis of their octahedral layer population. They suggested that the Mg in the Cheto-types leads to an ordered distribution with one fourth of the aluminum replaced by magnesium. In contrast, in the Wyoming-type montmorillonites the Mg content is lower, and the octahedral sites occupied by Mg are randomly distributed. The Mg average content in Cheto-type montmorillonites is in agreement with the Grim and Kulbicki hypothesis as shown in Table 3. The analysis of variance, however, shows Fe also to be a very important discriminant variable in the octahedral sheets, whereas its tetrahedral content is of very small significance. Finally, the interlayer content seems to play an important role in this discrimination through the Ca content which is significantly higher in Cheto-type montmorillonites (Tables 5 and 6).

Table 10. Analysis (7): whole population. Significance of the chemical variables, classification coefficients, unstandardized discriminant function coefficients, and canonical variables from analysis (7), whole population.

	Species or type	Function	Al^{IV}	Al^{VI}	Fe
Significance			0.000	0.000	0.000
Classification coefficients	Wyoming		−286.44	1736.77	1817.70
	Tatatilla		−268.19	1692.80	1746.23
	Otay-Chambers		−287.64	1725.36	1794.51
	'non-ideal' mont.		−278.33	1752.75	1853.34
	beidellite		−233.24	1690.55	1755.04
Unstandardized coefficients		1	−8.6988	7.6319	10.2540
		2	−0.5037	10.2282	19.2307
		3	7.3100	−1.8847	0.2885
		4	3.7563	−2.9889	−6.1098
Canonical variables		1	−0.6421	−0.4133	0.0807
		2	0.2115	−0.2554	0.7438
		3	0.5559	−0.5411	0.3300
		4	0.1847	0.0718	−0.2134

[1] The symbol * is used when the upward stepwise method does not include the element in the statistical analysis.
[2] Ω as in Table 3.

Schultz (1969) suggested a subdivision of Cheto-type montmorillonites into three different types: Otay-, Chambers-, and Tatatilla-types. These types are chemically characterized by a large net layer charge, which is almost entirely (85–100%) in the octahedral sheet in Otay-type samples, whereas in the Chambers- and Tatatilla-type samples, the octahedral charge is in the range 50–85% of the total layer charge. Multivariate factor analysis and discriminant analysis show that Tatatilla-type samples are strongly discriminated and seem to form a well-defined type within the Cheto-type group; whereas, according to the present data, a differentiation between the Chambers- and Otay-types is not as evident. A multivariate analysis therefore was carried out with the same samples but grouping the Otay-type samples with the Chambers-type samples; thus only five types of smectites were considered. The results are reported in Tables 9 and 10. The significance of discrimination and all other discriminative parameters as well as the significance of all chemical variables are much better than those found with Al-rich smectites subdivided into six groups. Only 4 samples of 75 were misclassified.

In conclusion, multivariate analysis of variance and discriminant analysis emphasize the differences in the crystal chemistry of types of Al-rich smectites proposed earlier on the basis of their physicochemical behavior. The strong significance found in discrimination allows a high probable attribution of a sample to the correct type, given the chemical analysis only.

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REFERENCES

Brigatti, M. F. (1983) Relationships between composition and structure in Fe-rich smectites: *Clay Miner.* **18,** 177–186.

Brigatti, M. F. and Poppi, L. (1981) A mathematical model to distinguish the members of the dioctahedral smectite series: *Clay Miner.* **16,** 81–89.

Byström Brusewitz, A. M. (1976) Studies on the Li test to distinguish between beidellite and montmorillonite: in *Proc. Int. Clay Conf., Mexico City, 1975,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 419–428.

Cooley, W. W. and Lohnes, P. R. (1971) *Multivariate Statistical Methods:* Wiley, New York, 364 pp.

Del Pennino, U., Mazzega, E., Valeri, S., Alietti, A., Brigatti, M. F., and Poppi, L. (1981) Interlayer water and swelling properties of monoionic montmorillonites: *J. Colloid Interface Sci.* **84,** 301–309.

Fripiat, J., Chaussidon, J., and Jelli, A. (1971) *Chimie-Physique des Phénomènes de Surface. Applications aux Oxydes et aux Silicates:* Masson et Cie, Paris, 260–296.

Greene-Kelly, R. (1953) The identification of montmorillonoids in clays: *J. Soil Sci.* **4,** 233–237.

Grim, R. E. and Kulbicki, G. (1961) Montmorillonite: high temperature reactions and classification: *Amer. Mineral.* **46,** 1329–1369.

Landgraf, K. F. (1979a) Röntgenographische Unterscheidung von Cheto- und Wyomingtyp bei Montmorilloniten nach den relativen Intensitäten der (00*l*) Serie des Glykolkomplexes: *Chemie der Erde* **38,** 233–244.

Landgraf, K. F. (1979b) Unterscheidung von Cheto- und Wymoingtyp bei Montmorilloniten nach dem Lichtbrechungseffekt organischer Zwischenschichten: *Chemie der Erde* **38,** 97–104.

Mahalanobis, P. C. (1936) On the generalized distance in statistics: *Proc. Nat. Inst. Sci. India* **12,** 49–55.

Morrison, D. F. (1978) *Multivariate Statistical Methods:* McGraw-Hill, Auckland, 414 pp.

Nie, N. H., Hadlai Hull, C., Jenkins, J. G., Steinbrenner, K., and Bent, D. H. (1975) *SPSS Statistical Package for the Social Sciences:* McGraw-Hill, New York, 675 pp.

Novák, I. and Čičel, B. (1978) Dissolution of smectites in hydrochloric acid: II. Dissolution rate as a function of cristallochemical composition: *Clays & Clay Minerals* **26,** 341–344.

Table 10. Continued.

Mg	Mn	Ti	Ca	Na	K	Ω^2	Constant
0.000	0.034	0.073	0.000	0.154	0.294	0.031	
1339.99	4690.20	2118.44	−49.25	*	172.53	−43.25	−1697.25
1312.34	4028.22	2071.80	1.91	*	169.64	−41.98	−1619.17
1357.38	4742.18	2188.22	−45.12	*	155.78	−43.05	−1683.20
1370.57	4949.62	2176.62	−50.34	*	147.02	−44.03	−1741.89
1289.98	4104.75	2114.42	−20.51	*	204.51	−42.11	−1619.95
12.3662	127.6909	13.6553	−5.2564	*	−8.4689	−0.2225	
5.5507	115.2773	2.8803	−6.9972	*	−1.1564	−0.3281	
4.4554	4.2594	19.6277	3.9793	*	−5.4682	−0.0619	
0.5281	90.8235	40.2093	−11.3230	*	6.5898	0.0388	
0.5780	0.1144	0.0965	−0.0331	*	−0.0996	−0.1721	
−0.3059	0.0597	0.0486	−0.2976	*	0.0789	0.1274	
0.6351	0.3259	0.1318	0.4907	*	0.0273	−0.0365	
0.0716	−0.0719	0.4891	−0.6709	*	0.2416	0.0924	

Poppi, L. and Brigatti, M. F. (1976) Cristallochimica e caratteristiche termiche di alcune montmorilloniti italiane: *Mineral. Petrogr. Acta* **21,** 43–52.

Prost, R. (1976) Interaction between adsorbed water molecules and the structure of clay mineral: hydration mechanism of smectites: in *Proc. Int. Clay Conf., Mexico City, 1975,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 351–359.

Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group, their origin and relation to soils and clays: *U.S. Geol. Surv. Prof. Pap.* **205-B,** 23–79.

Rozenson, I. and Heller-Kallai, L. (1977) Mössbauer spectra of dioctahedral smectites: *Clays & Clay Minerals* **25,** 94–101.

Russell, J. D. and Clark, D. R. (1978) The effect of Fe- for Si substitution on the *b*-dimension of nontronite: *Clay Miner.* **13,** 133–137.

Schomburg, J. (1976) Dilatometrische Untersuchungen an dioktaedrischen Smektiten: *Chemie der Erde* **35,** 192–198.

Schultz, L. G. (1969) Lithium and potassium absorption, dehydroxylation temperature, and structural water content of aluminous smectites: *Clays & Clay Minerals* **17,** 115–149.

SPSS-X Statistical Algorithms (1983) SPSS Inc., Chicago, Illinois.

Weir, A. H. and Greene-Kelly, R. (1962) Beidellite: *Amer. Mineral.* **47,** 137–146.

Wilks, S. S. (1932) Certain generalizations in the analysis of variance: *Biometrika* **24,** 471–494.

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