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NOTES

SUBSTITUTION OF IRON AND TITANIUM IN KAOLINITES

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Iron and titanium may be present in kaolinites as discrete mineral species and/or in the structure of kaolinites substituting for Al or Si. Mössbauer (Malden and Meads, 1967) and ESR (Angel and Hall, 1972; Meads and Malden, 1975) techniques have provided evidence that ferric iron exists as a constituent in the octahedral layer of kaolinites. Rengasamy *et al.* (1975b) reported the chemical composition of soil kaolinites calculated from selective dissolution data. When the extracted Fe^{3+} content was included in the octahedral composition, the SiO_2/R_2O_3 molar ratio was very close to the ideal ratio of 2.00. Electron microprobe studies (Jepson and Rowse, 1975) have shown that both Fe and Ti occur possibly as isomorphous constituents in kaolinite. Substituted Ti can be distinguished from Ti oxides in a scheme of selective dissolution using hydrofluotitanic acid (Dolcater *et al.*, 1970).

During characterization of six sedimentary kaolinites, the author combined several techniques to obtain the elemental compositions of the kaolinites and their relation to the *b*-parameters of the minerals.

The kaolinites (< 2 μm) were dehydroxylated after removal of amorphous ferri–alumino silicates, followed by selective dissolution as described by Rengasamy *et al.* (1975b). Si, Al and Fe were determined in the extracts by colorimetry. Total Fe and Ti in the amorphous free-clay fractions were determined by X-ray fluorescent spectrography (Norrish and Hutton, 1969). Free TiO_2 was determined using hydrofluotitanic acid (Dolcater *et al.*, 1970). The clay fractions were analysed for Fe^{2+} by the method of Roth *et al.* (1968). The spectrographic analyses for Ti and Fe agreed well with those obtained by chemical methods. The difference between total Ti and Ti present as free oxide was allocated to the atomic structures of the kaolinites.

The mineralogical composition of the amorphous free-clay fractions (Table 1) was determined and used to calculate the unit cell cation composition of the kaolinites (Rengasamy *et al.*, 1975 a,b). Since Fe^{2+} contents of the clays were found to be negligible, Fe^{3+} was the form assumed to be present in the octahedra of kaolinites. Ti, not present as free TiO_2 (expressed as rutile and anatase in Table 1), was also allocated to the octahedral positions since the Si content of the minerals was equal to, or in excess of, the Si content of ideal kaolinite. The Ti in the octahedra was assumed to be trivalent so that the layer-charge distribution of ideal kaolinite was retained. Ti^{3+} occurs in stable octahedral geometry in Ti_2O_3, which is analogous to corundum.

Fe^{3+} and Ti^{3+} content almost satisfied the deficiency in Al content in the octahedra of these kaolinites, giving SiO_2/R_2O_3 molar ratios very close to the value of 2.00 (Table 2). The validity of the unit cell composition is dependent on the accuracy of the analytical methods. However, the agreement between chemical and spectrographic methods, the small deviation of SiO_2/R_2O_3 molar ratios from 2.00, and the linear relation between the *b*-parameter and Al in the unit cell composition of the octahed-

Table 1. Mineralogical composition (%) of the amorphous free-clay (< 2 μm) fractions

No.	Sample	Kaolinite	Quartz	Mica	Smectite	Rutile + Anatase	Total
1.	New Zealand kaolin	96.2	3.8	0.3	0.1	0.7	101.1
2.	Malone kaolin	93.0	2.0	2.6	0.4	1.1	99.1
3.	Georgia kaolin	98.2	0.3	0.5	2.0	0.4	101.4
4.	Montana kaolin	97.4	2.6	0.6	0.2	0.8	101.6
5.	New Mexico kaolin	99.0	1.0	0.4	0.2	0.4	101.0
6.	Kaolinite, India	91.8	4.6	1.3	1.6	0.5	99.8

Table 2. Constituents, molar ratio, unit cell cation composition and *b*-parameters of the kaolinites

	Constituents estimated						
No.	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Ti_2O_3 (%)	Molar ratio SiO_2/R_2O_3*	Unit cell cation composition	*b*-parameter (Å)
1.	44.74	37.19	0.58	0.29	2.01	$Si_{4.00}Al_{3.93}Fe_{0.04}Ti_{0.02}$	8.924
2.	43.26	35.13	0.98	0.65	2.02	$Si_{4.02}Al_{3.86}Fe_{0.07}Ti_{0.05}$	8.935
3.	45.67	36.17	1.13	1.28	2.05	$Si_{4.04}Al_{3.78}Fe_{0.08}Ti_{0.10}$	8.945
4.	45.29	37.94	0.48	0.22	2.00	$Si_{4.00}Al_{3.95}Fe_{0.03}Ti_{0.02}$	8.914
5.	46.03	38.09	0.96	0.38	2.00	$Si_{4.00}Al_{3.91}Fe_{0.06}Ti_{0.03}$	8.928
6.	42.68	34.75	1.65	0.14	2.01	$Si_{4.01}Al_{3.85}Fe_{0.13}Ti_{0.01}$	8.940

* R_2O_3 includes Al_2O_3, Fe_2O_3, and Ti_2O_3.

ral layers ($Y = 9.064–0.173x$, $\gamma = -0.96^{**}$) all indicate the substitution of Fe and Ti in the octahedra of the minerals examined.

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