

ISOMORPHOUS SUBSTITUTION OF IRON FOR ALUMINIUM IN SOME SOIL KAOLINITES

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Abstract—Clay (<2 μm) and fine silt (2–20 μm) fractions of twenty seven soil samples from eight tropical ferruginous profiles of the Mysore Plateau (India) were analysed for kaolinite by dehydroxylation and selective dissolution. The considerable amounts of iron extracted by the procedure and the closeness of the $\text{SiO}_2/\text{R}_2\text{O}_3$ molar ratios (2.00–2.18) to the ideal value of 2.00 indicated that iron was a structural constituent of the kaolinites. The calculated unit cell cation composition of the kaolinites showed a substitution of 0.11–0.82 atoms of Fe(III) for Al in every four octahedral sites. The kaolinites in these soils appear to be products of crystallization from weathering solutions.

INTRODUCTION

The chemical analyses of kaolinite have been reported to conform very closely with the ideal formula $(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}$ (Ross and Kerr, 1931; Grim, 1968). Reports of deviations from this composition, apart from the high-silica mineral anauxite (Hendricks, 1936), have been very rare. Anauxite itself is now believed to be a mixture of silica and kaolinite (Langston and Pask, 1968; Bailey and Langston, 1969).

In the kaolinite structure isomorphous substitution leading to a permanent negative charge has been suggested (Schofield, 1949; Sumner, 1963). Youell (1958) indicated the possible existence of a series between dioctahedral kaolinite and trioctahedral chamosite, with varying degrees of substitution of Fe for Al. Mössbauer studies of some iron-rich kaolinites (Weaver *et al.*, 1967; MacKenzie, 1969) also have led to the speculation that Fe(III) might occur in the octahedral layer. The homogeneous distribution of Fe in a kaolinite, as found by electron microprobe analysis (Weaver, 1968), was interpreted to indicate that some Fe was present in the kaolinite structure. An interesting occurrence of Cr(III) substituting for some Al in a kaolinite formed by hydrothermal alteration of ultramafic rocks was reported by Maksimovič and Crnkovič (1968). Robertson *et al.* (1954) published the only analytically substantiated investigation of isomorphous substitution in kaolinites. Two kaolinites from Tanganyika showed isomorphous substitution of Al for Si in the tetrahedral layer and Mg and Fe(III) for Al in the octahedral layer giving the cation composition $(\text{Si}_{1.982}\text{Al}_{0.018})(\text{Al}_{1.958}\text{Fe}_{0.039}^{3+}\text{Mg}_{0.003})$. The cation exchange capacity agreed closely with the calculated layer charge.

The authors have not found any report on the chemical composition of soil kaolinites. Though direct analysis is not possible, selective dissolution with 0.5 N NaOH of dehydroxylated clay (Hashimoto and Jackson, 1960) can be used to determine the chemical

composition of kaolinites when other unstable minerals are absent.

During a study of the mineralogy of some kaolinitic soils of India, it was found that iron was also being extracted by the above procedure. This report embodies the results of an investigation into the chemical composition of the kaolinites in these soils.

METHODS

Twenty seven samples* from eight ferruginous soil profiles in the districts of Bangalore and Kolar ($13^\circ 15' - 13^\circ 45' \text{N}$; $78^\circ - 78^\circ 30' \text{E}$) of the Mysore Plateau (India) were dispersed and the clay (<2 μm) and fine silt (2–20 μm) fractions separated (Jackson, 1969). The fractions were freed of amorphous minerals (Hashimoto and Jackson, 1960) and subjected to a further removal of free iron oxides with citrate-bicarbonate-dithionite (CBD) according to the procedure given by Mehra and Jackson (1960).

An aliquot of each amorphous mineral-free fraction was K^+ -saturated, washed and dried. A weighed portion was heated at 550°C for 4 hr and the calcined residue subjected to a further 0.5 N NaOH treatment followed by CBD extraction. Both extracts were analyzed colorimetrically for Si (Jackson, 1958), Al (Krishna Murti *et al.*, 1974) and Fe (Krishna Murti *et al.*, 1970).

The clay fractions were analyzed for Fe(III) and Fe(II) by the method of Roth *et al.* (1968).

RESULTS AND DISCUSSION

The clay and silt fractions were dominantly kaolinitic with appreciable quantities of amorphous material (Rengasamy *et al.*, 1975).

Halloysite could not be detected in electron micrographs. The amounts of Si, Al and Fe (as oxides) extracted by NaOH and CBD reagent after dehydroxylation of the kaolinite in the clay and fine silt fractions are given in Table 1. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar

* Complete description of the soil profiles was reported by Rengasamy (1973).

Table 1. Constituents extracted by 0.5 N NaOH and subsequent CBD treatment from amorphous-free clay (<2 μm) and fine silt (2–20 μm) fractions after dehydroxylation

Sample Number	Horizon	Depth cm	Clay (<2 μm) fraction					Fine silt (2–20 μm) fraction					
			Constituents extracted			Molar ratios		Constituents extracted			Molar ratios		
			SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ /Al ₂ O ₃	SiO ₂ /R ₂ O ₃	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ /Al ₂ O ₃	SiO ₂ /R ₂ O ₃	
Profile 1. Nandi series													
S184	A	0–25	33.35	25.20	4.65	2.24	2.01	8.50	6.20	1.00	2.33	2.11	
S185	B ₁	25–100	36.15	26.85	5.35	2.29	2.03	8.75	6.20	1.00	2.41	2.18	
S186	C	100–180+	30.00	23.05	3.55	2.21	2.02	31.65	23.80	1.30	2.25	2.18	
Profile 2. Chikballapur series													
S178	A _p	0–13	28.10	21.00	3.75	—	2.27	2.04	15.80	11.60	2.20	2.31	2.06
S179	B ₁₁	13–65	31.20	24.00	3.75	—	2.22	2.02	10.30	7.05	1.90	2.48	2.12
S180	B ₂₁	65–104	34.05	26.30	3.90	—	2.19	2.01	6.05	3.85	1.55	2.66	2.12
S181	B _{en}	104–150+	36.50	28.10	3.90	—	2.21	2.03	25.80	19.15	2.15	2.29	2.14
Profile 3. Muddhanahalli ravine cut													
S187	B ₁	0–90	37.45	30.40	2.05	—	2.09	2.00	10.20	7.95	0.95	2.18	2.02
S188	B _{en}	90–120	35.25	26.20	5.90	—	2.28	2.00	38.85	29.60	2.90	2.23	2.10
S189	BL ₂	120–320	40.45	31.55	4.05	—	2.18	2.01	36.40	28.25	2.35	2.19	2.08
S190	BL ₄	320–620	37.90	29.90	3.00	—	2.15	2.03	37.25	29.40	1.35	2.15	2.09
S191	C	620+	39.95	31.00	3.40	—	2.19	2.04	35.75	28.40	1.75	2.14	2.06
S193	BL ₄	—	40.90	29.75	6.75	—	2.33	2.04	38.95	30.70	3.20	2.15	2.02
Profile 4. Vijayapur series													
S172	A	0–22	20.90	14.80	4.70	—	2.40	1.99	5.35	4.05	0.45	2.23	2.08
S173	B ₁	22–136	19.00	13.90	2.60	—	2.33	2.08	4.35	3.20	0.45	2.31	2.11
S174	B _{en}	136+	30.85	24.10	3.30	—	2.17	2.00	13.30	9.85	1.20	2.29	2.13
Profile 5. Koppalli series													
S194	A _p	0–13	36.00	26.55	5.60	—	2.31	2.03	12.30	9.45	1.25	2.21	2.04
S195	B ₁	13–53	35.60	24.85	8.30	—	2.43	2.00	16.30	12.50	1.80	2.23	2.04
S196	B ₃	53–107+	37.90	26.60	6.55	—	2.42	2.11	25.90	18.40	3.85	2.39	2.11
Profile 6. Royalpad series													
S198	A _p	0–30	34.45	23.70	8.25	—	2.46	2.02	8.05	5.85	1.15	2.34	2.07
S199	B ₂₁	30–78	32.45	22.50	7.65	—	2.44	2.01	11.70	8.95	1.30	2.22	2.03
S200	B ₂₃	78–140+	33.00	23.30	6.20	—	2.41	2.06	20.05	14.75	1.85	2.31	2.14
Profile 7. Nandi Cross													
S182	A	0–60	33.50	25.30	4.25	—	2.24	2.02	24.10	18.45	2.25	2.22	2.06
S183	BL ₂ -b	60–150+	38.45	30.00	4.05	—	2.17	2.00	39.95	31.75	3.25	2.14	2.01
Profile 8. Malmachanahalli series													
S175	A _p	0–20	23.30	17.35	3.40	—	2.29	2.03	9.90	7.25	0.85	2.32	2.16
S176	B ₂	20–75	23.00	17.15	3.35	—	2.27	2.02	3.65	2.75	0.30	2.24	2.08
S177	B ₈	75–140	13.30	8.55	2.95	—	2.64	2.16	1.40	1.05	0.20	2.24	2.00

ratios varied from 2.10 to 2.64, in most cases significantly higher than the 2.00 for kaolinite of ideal composition. However, the SiO₂/Al₂O₃ + Fe₂O₃ molar ratios came out to be strikingly close to the ideal value of 2.00 (mean value 2.03 for clays and 2.09 for silts), which strongly suggested that the iron was a structural component of the kaolinites.

The unit cell cation composition of the kaolinites was calculated by an adaptation of Kelley's (1955) procedure for montmorillonites. For this, the selective dissolution analyses data given in Table 1 were used, and the total cationic equivalents was taken to be 28 which is the total negative charge per unit cell formula weight. Iron was assumed to be in the trivalent form. All the Fe³⁺ and Al were assigned to the octahedral layer (4 moles). In most samples there was slightly more SiO₂ than four moles of silica would account for. The appropriate amount of SiO₂ was assigned to the tetrahedral layer and the excess silica (0.2–6.3 per cent) reported as such. Presumably a small amount of the free silica in the original samples is not removed by the first treatment with 0.5 N NaOH but is extracted by the second. Langston and Jenne (1964) reported that free SiO₂ could not be completely removed from kaolinites by alkali extraction and that SiO₂ continued to be extracted by alkali in successive treatments. The kaolinite content of each sample was calculated from the theoretical content of 46.5 per cent SiO₂. Table 2 gives the unit cell

composition of the soil kaolinites and the excess SiO₂ values. The analyses data clearly indicate an isomorphous substitution of iron for aluminium in the octahedral layer in the range of 0.11–0.82 in every four octahedral positions.

The *b*-parameters calculated from the (060) spacing data available for eighteen samples on the basis of the triclinic cell of Brindley and Robinson (1946) gave a significant positive correlation with the octahedral Fe³⁺ content (Fig. 1).

Briner and Jackson (1970) proposed a SiO₂/R₂O₃ molar ratio method of calculation to eliminate the interference by other iron-rich phyllosilicates such as partially chloritized montmorillonites which may be dehydroxylated along with kaolinite. El-Attar and Jackson (1973) reported that large quantities of silica and alumina were dissolved from 2:1 layer silicates by the 0.5 N NaOH extraction after dehydroxylation of the clay fractions of montmorillonitic soils in Nile River sediments. This was reflected in the high SiO₂/R₂O₃ molar ratios of 2.44–3.34 obtained by them.

In the clays and silts analyzed for this study the SiO₂/R₂O₃ molar ratios of the constituents dehydroxylated by the heat treatment at 550°C were very close to 2.00. It is a reasonable conclusion that only kaolinite was dissolved by the procedure. Further, the total iron content of the clays was approximately equal to the sum of the iron content of the amorphous mineral components and of the kaolinite, and

Table 2. Kaolinite content and unit cell cation composition of the kaolinites in the amorphous-free clay and fine silt fractions

Sample Number	Clay fraction				Fine silt fraction			
	Calculated SiO ₂ %	Excess SiO ₂ %	Kaolinite		Calculated SiO ₂ %	Excess SiO ₂ %	Kaolinite	
			Content %	Unit cell cation composition			Content %	Unit cell cation composition
S184	33.10	0.25	71.2	Si ₄ Al _{3.58} Fe _{0.42}	8.05	0.45	17.3	Si ₄ Al _{3.62} Fe _{0.38}
S185	35.60	0.55	76.6	Si ₄ Al _{3.55} Fe _{0.45}	8.00	0.75	17.2	Si ₄ Al _{3.63} Fe _{0.37}
S186	29.75	0.25	64.0	Si ₄ Al _{3.64} Fe _{0.36}	29.05	2.60	62.5	Si ₄ Al _{3.86} Fe _{0.14}
S178	27.50	0.60	59.2	Si ₄ Al _{3.59} Fe _{0.41}	15.30	0.50	32.9	Si ₄ Al _{3.56} Fe _{0.44}
S179	31.05	0.15	66.7	Si ₄ Al _{3.64} Fe _{0.36}	9.70	0.60	20.9	Si ₄ Al _{3.42} Fe _{0.58}
S180	33.85	0.20	72.8	Si ₄ Al _{3.66} Fe _{0.34}	5.70	0.35	12.2	Si ₄ Al _{3.18} Fe _{0.82}
S181	35.95	0.55	77.3	Si ₄ Al _{3.68} Fe _{0.32}	24.10	1.70	51.9	Si ₄ Al _{3.75} Fe _{0.27}
S187	37.30	0.15	80.2	Si ₄ Al _{3.84} Fe _{0.16}	10.10	0.10	21.7	Si ₄ Al _{3.71} Fe _{0.29}
S188	35.25	0.00	75.8	Si ₄ Al _{3.50} Fe _{0.50}	37.00	1.85	79.5	Si ₄ Al _{3.77} Fe _{0.23}
S189	40.15	0.30	86.3	Si ₄ Al _{3.70} Fe _{0.30}	35.00	1.40	75.2	Si ₄ Al _{3.80} Fe _{0.20}
S190	37.40	0.50	80.4	Si ₄ Al _{3.76} Fe _{0.24}	35.65	1.60	76.6	Si ₄ Al _{3.80} Fe _{0.11}
S191	39.00	0.95	83.9	Si ₄ Al _{3.74} Fe _{0.26}	34.70	1.05	74.6	Si ₄ Al _{3.85} Fe _{0.15}
S193	40.10	0.80	86.2	Si ₄ Al _{3.49} Fe _{0.51}	38.55	0.40	82.8	Si ₄ Al _{3.75} Fe _{0.25}
S172	20.90	0.00	44.9	Si ₄ Al _{3.33} Fe _{0.67}	5.10	0.25	11.0	Si ₄ Al _{3.73} Fe _{0.27}
S173	18.25	0.75	39.2	Si ₄ Al _{3.57} Fe _{0.43}	4.10	0.25	8.8	Si ₄ Al _{3.66} Fe _{0.34}
S174	30.85	0.00	66.3	Si ₄ Al _{3.68} Fe _{0.32}	12.50	0.80	26.9	Si ₄ Al _{3.71} Fe _{0.29}
S194	35.45	0.55	76.2	Si ₄ Al _{3.53} Fe _{0.47}	12.05	0.25	25.9	Si ₄ Al _{3.69} Fe _{0.31}
S195	35.45	0.15	76.2	Si ₄ Al _{3.30} Fe _{0.70}	16.05	0.25	34.5	Si ₄ Al _{3.66} Fe _{0.34}
S196	36.20	1.70	77.8	Si ₄ Al _{3.46} Fe _{0.54}	24.50	1.40	52.7	Si ₄ Al _{3.53} Fe _{0.47}
S198	34.10	0.35	73.3	Si ₄ Al _{3.27} Fe _{0.73}	7.75	0.30	16.7	Si ₄ Al _{3.55} Fe _{0.45}
S199	32.25	0.20	69.3	Si ₄ Al _{3.29} Fe _{0.71}	11.55	0.15	24.8	Si ₄ Al _{3.66} Fe _{0.34}
S200	32.05	0.95	68.9	Si ₄ Al _{3.42} Fe _{0.58}	18.70	1.35	40.3	Si ₄ Al _{3.71} Fe _{0.29}
S182	33.00	0.50	70.9	Si ₄ Al _{3.61} Fe _{0.39}	23.40	0.70	50.3	Si ₄ Al _{3.71} Fe _{0.29}
S183	38.45	0.00	82.7	Si ₄ Al _{3.68} Fe _{0.32}	39.95	0.00	86.0	Si ₄ Al _{3.74} Fe _{0.26}
S175	22.95	0.35	49.3	Si ₄ Al _{3.46} Fe _{0.54}	9.15	0.75	19.6	Si ₄ Al _{3.72} Fe _{0.28}
S176	22.70	0.30	48.8	Si ₄ Al _{3.50} Fe _{0.50}	3.45	0.20	7.5	Si ₄ Al _{3.72} Fe _{0.28}
S177	12.25	1.05	26.3	Si ₄ Al _{3.28} Fe _{0.72}	1.40	0.00	3.0	Si ₄ Al _{3.59} Fe _{0.41}

the ferrous iron in the fractions (Table 3). The small amounts of Fe²⁺ found in the samples (0.16–0.28% as Fe₂O₃) may be a constituent of the micaceous minerals. The iron in these kaolinites was, therefore, chiefly in the trivalent form so that the layer charge distribution of ideal kaolinite was retained.

Electron microscopic examination of the kaolinite flakes after removal of amorphous minerals from both the clays and the silts showed the individual flakes to be as small as 0.01 μm across. The small size of the kaolinite flakes and the varying amounts of iron present in kaolinites from different horizons of the

Table 3. Forms of iron in the soil clays (oven-dry clay weight basis)

Sample Number	Total iron (as Fe ₂ O ₃) content of clay %	Forms of iron (as Fe ₂ O ₃)			Total %
		Fe(II) content of clay %	Fe(III) content of AFAS* %	Fe(III) content of kaolinite %	
S184	4.65	0.25	1.00	3.40	4.65
S185	5.30	0.20	1.20	3.80	5.20
S186	3.60	0.20	0.65	2.70	3.55
S178	3.80	0.20	0.85	2.80	3.85
S179	4.00	0.15	1.00	2.75	3.90
S180	4.00	0.15	1.10	2.80	4.05
S181	4.00	0.15	0.75	2.90	3.80
S187	2.70	0.30	0.85	1.45	2.60
S188	7.00	0.15	2.25	4.35	6.75
S189	6.10	0.15	2.70	3.25	6.10
S190	3.60	0.15	1.00	2.70	3.85
S191	3.60	0.15	0.55	2.95	3.65
S193	10.90	0.15	5.25	5.40	10.80
S172	4.70	0.30	0.90	3.55	4.75
S173	3.15	0.20	1.15	1.85	3.20
S174	4.00	0.20	1.25	2.45	3.90
S194	4.65	0.15	0.70	3.65	4.55
S195	6.40	0.15	1.00	5.00	6.15
S196	5.15	0.15	0.65	4.25	5.05
S198	7.30	0.20	1.05	6.00	7.25
S199	6.90	0.20	1.25	5.35	6.80
S200	5.95	0.20	1.25	4.25	5.70
S182	4.00	0.30	0.80	2.85	3.95
S183	4.45	0.15	0.65	3.45	4.25
S175	5.20	0.20	2.45	2.65	5.30
S176	4.80	0.25	1.90	2.65	4.80
S177	3.80	0.25	1.00	2.60	3.85

* Amorphous ferri-aluminosilicates.

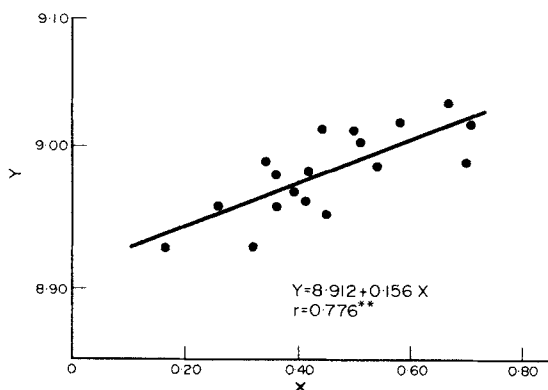


Fig. 1. The relation between b -parameter of the kaolinites (Y) and number of Fe^{3+} cations (X) in the formula $\text{Si}_4(\text{Al}_{4-x}\text{Fe}_x^{3+})\text{O}_{10}(\text{OH})_8$.

same profile strongly suggest that the minerals originated by crystallization from weathering solutions.

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