Transformation of short-range order minerals in maize (*Zea mays* L.) rhizosphere

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ABSTRACT

Under nutrient stress, low molecular weight organic acids are released in rhizosphere, which dissolve the crystalline layered silicate minerals and subsequently some short range order (SRO) minerals may be formed. To analyze this hypothesis, a controlled greenhouse experiment was conducted with three contrasting soils belonging to Alfisols, Inceptisols and Vertisols order in two phases, viz. Sorghum-sudangrass depletion and test crop experiment on maize. The SROs were measured by selective dissolutions. The results indicate that, NaOH extractable amorphous ferri-alumino silicate was higher in rhizosphere, whereas mild extractant extractable SRO dissolution was increased due to fertilization and rhizospheric effect. Fourier transform infrared band showed changes in 3400–3600/cm region (adsorbed water) and Si-O stretching vibration (1000/cm). This information will provide a new insight in formation of SROs under the rhizospheric environment.

Keywords: amorphous ferri-alumino silicate; low molecular weight organic acid; Alfisols; Inceptisols; Vertisols

The clay fraction (< 2 μm) of soils contains appreciable quantities of free and combined oxides of Si, Al and Fe, which are amorphous to X-rays (Krishna Murti et al. 1976), are known as short-range order (SRO) minerals; there are for instance, allophane, imogolite, ferrihydrite, hisingerite, amorphous Fe and Al oxides, hydroxides. They are also known as natural nano-materials (Theng and Yuan 2008); because of their too small particle size (< 100 nm) in at least one dimension (Holister et al. 2003).

When plants are grown intensively in a small amount of soil under nutrient stress condition, they release low molecular weight organic acids (LMWOAs) (Young et al. 1998). Plants excrete LMWOAs into the soil to increase the solubility of nutrients (e.g. P), detoxify metals (e.g. Al^{3+}), aid in chemotactic responses and the formation of symbiotic associations (Dakora and Philips 2002). Under P-stress condition, maize releases mono- (acetic, formic, glycolic and lactic), di- (malic, oxalic and succinic) and tri- (citric and *trans*-aconitic) carboxylic organic acids (Gaume et al. 2001). Out of these malic, succinic, citric

and trans-aconitic acids are released in higher amount (Gaume et al. 2001). The concentration of organic acids in soil solution is low (10^{-3} to 4×10^{-4} mol/L), but greater amounts are found in plant rhizosphere (Vance et al. 1996). These acids interact with the hydrolytic products of Al and Fe and form organo-mineral precipitates (Vance et al. 1996). Since these complexes with Al and Fe are stable in nature, their formation disrupts the crystallization of Al hydroxides and promotes the formation of SRO Al hydroxides (Colombo et al. 2004). Keeping the above facts in view, an experiment was conducted to characterize SROs formed in maize rhizosphere supplied with various levels of P and K under controlled environment.

MATERIAL AND METHODS

Three surface (0–15 cm) soil samples representing Alfisols (Typic Haplustalfs), Inceptisols (Typic Haplustept) and Vertisols (Typic Haplustert) were used for the present study. In the first phase of the ex-

periment, an exhaustive crop, Sorghum-sudangrass hybrid (cv. Multicut GSC-40) was grown for 100 days in one part of the soil to deplete it from P and K. In the second phase, maize (cv. HPQM-1) was grown intensively in 2 kg of soil for 60 days after germination. Nitrogen fertilization was given 80 mg/kg N uniformly to all the treatments. Three levels of nutrient status, therefore, were maintained viz. Sorghum-sudangrass pre-depleted soil (depleted), original soil (original), and original soil + 40 mg/kg P + 40 mg/kg K (fertilized). Similarly treated soil without any plant was also kept as non rhizosphere, thus, two rhizospheric status (rhizosphere and non rhizosphere) were created.

After the completion of pot experiment, soils were collected and processed. The fractionation of soil was done by removal of all binding agents (humus free clay) and without removal of all binding agents (clay-humus complex). Clay was separated by following Stokes' law. The collected clay suspension was centrifuged at 5000 rpm for 12 min to separate colloidal (< 0.2 µm) and non-colloidal (0.2–2 µm) fraction (Jackson 1975). Selective dissolution of SROs in humus free clay and clay-humus complex was performed by 4 methods: (1) Boiling with 200 mL 0.5 mol/L NaOH; (2) 0.2 mol/L acid ammonium oxalate (pH 3); (3) dithionite-citrate-bicarbonate (DCB), and (4) 0.1 mol/L sodium pyrophosphate (pH 10) and extracted SiO_2, Al_2O_3 and Fe_2O_3 concentrations were measured. From these concentrations, different parameters viz. amorphous ferri-alumino silicate (AFAS), oxalate extractable total oxide (TOX), oxalate extractable allophane plus imogolite (OEAI), crystalline iron (CRFE), poorly ordered iron (POFE), organically bound aluminum (OBAL), and organically bound iron (OBFE, Blakemore et al. 1981) were calculated. Infrared spectroscopy of the powdered samples was carried out by using the Bruker: ALPHA, FTIR/ATR system (typically 24 scans, resolution – 4/cm) in the region of 4000–400/cm. Differences in treatments means were tested by analysis of variance under factorial complete randomized design using MSTAT-C software (East Lansing, USA) and compared at the $P < 0.05$ level using *LSD* for all the parameters, as per statistical procedure outlined by Cochran and Cox (1992).

RESULTS

Chemical analysis of colloidal clay. Mean AFAS content of depleted and original fertility status was

Table 1. Effect of soil, fertility and rhizospheric status on amorphous ferri-alumino silicate (AFAS) and total oxide (TOX) in colloidal clay

Fertility status	Alfisols		Inceptisols		Vertisols		Mean
	NR	R	NR	R	NR	R	
AFAS (%)							
Depleted	11.05	11.58	16.22	16.14	14.21	15.80	14.17[A]
Original	11.51	12.92	16.67	16.70	13.44	14.11	14.22[A]
Fertilized	11.62	11.10	15.34	14.06	13.42	14.62	13.36[B]
Mean	11.39[F]	11.87[E]	16.07[A]	15.63[B]	13.69[D]	14.84[C]	
	11.63[C]		15.85[A]		14.27[B]		
LSD (*P* = 0.05), S × F × R = 0.37							
TOX (%)							
Depleted	1.58	1.76	2.45	2.45	1.92	1.98	2.03[B]
Original	1.83	1.80	2.39	2.08	2.03	1.93	2.01[B]
Fertilized	2.23	2.21	3.72	2.54	2.12	2.41	2.54[A]
Mean	1.88[D]	1.93[D]	2.85[A]	2.36[B]	2.02[C]	2.11[C]	
	1.90[C]		2.60[A]		2.07[B]		
LSD (*P* = 0.05), S × F × R = 0.17							

Means followed by the same letter within a row or column are not significantly different at 0.05 level of probability by *LSD* range test. R – rhizosphere; NR – non-rhizosphere; S – soil; F – fertility status; R – rhizospheric status
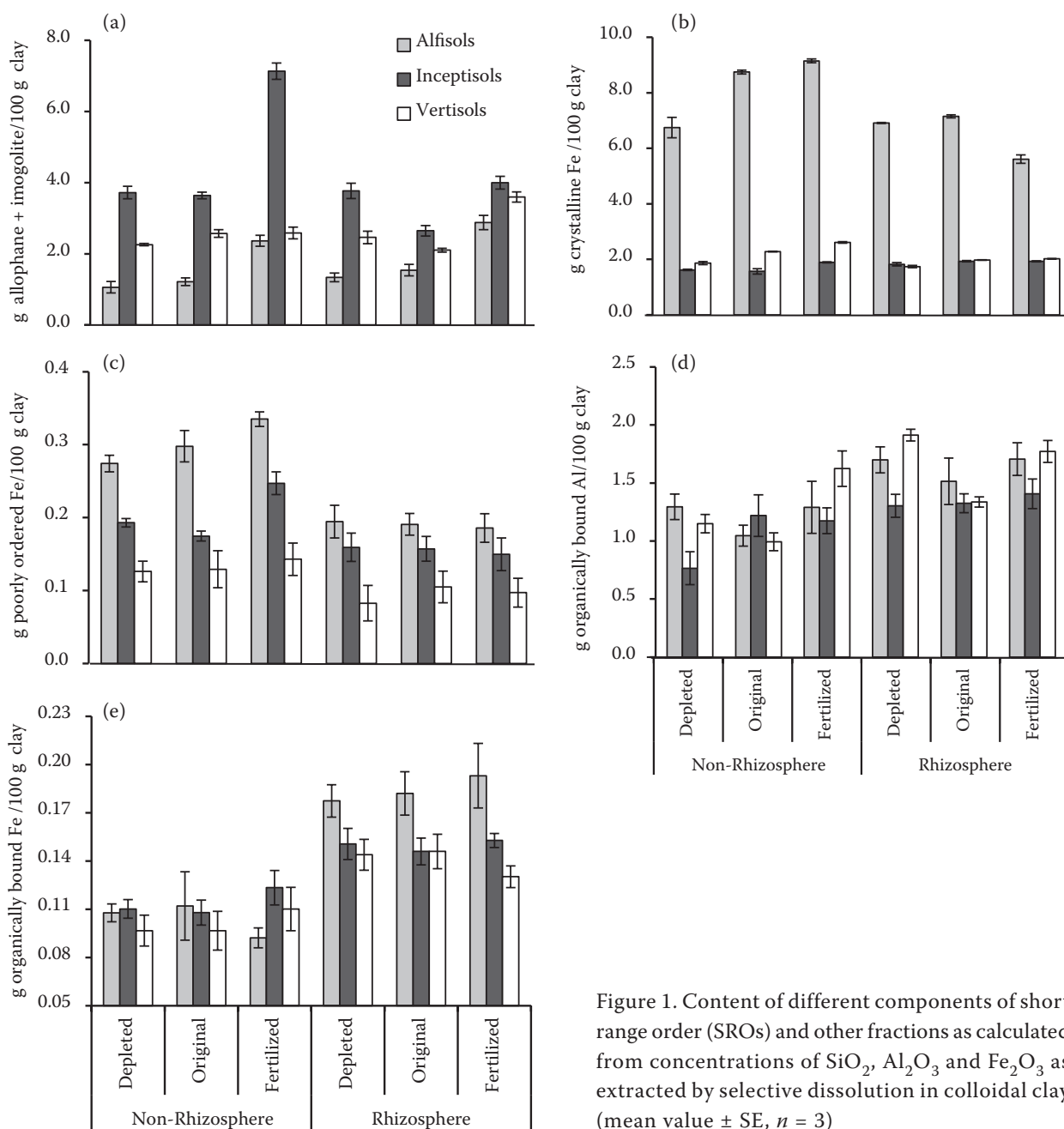
Figure 1. Content of different components of short range order (SROs) and other fractions as calculated from concentrations of SiO_2, Al_2O_3 and Fe_2O_3 as extracted by selective dissolution in colloidal clay (mean value ± SE, n = 3)

significantly higher than fertilized fertility status. Inceptisols contained significantly higher AFAS than Vertisols and Alfisols. The AFAS content of Alfisols × rhizosphere and Vertisols × rhizosphere were significantly higher than the same combinations with non-rhizosphere (Table 1). Maximum TOX was recorded in fertilized and Inceptisols treatments. Amount of TOX in Inceptisols × non-rhizosphere was higher than Inceptisols × rhizosphere. The rhizospheric effect was not significant in Vertisols and Alfisols (Table 1). OEAI did not differed significantly with fertility status. It followed the order Inceptisols > Vertisols > Alfisols. Inceptisols × non-rhizosphere contained more OEAI than Inceptisols × rhizosphere. No significant difference was observed in case of Vertisols (Figure 1a). CRFE was much high in Alfisols. Non-rhizosphere and rhizosphere differed significantly in mean CRFE. Among the interactions, Alfisols × non-rhizosphere resulted in maximum formation (Figure 1b). POFE (Figure 1c) was significantly higher in Alfisols followed by Inceptisols and Vertisols; and non-rhizosphere followed by rhizosphere. This was highest in fertilized × Alfisols which was at par with original × Alfisols. OBAL was highest in fertilized fertil-

Table 2. Effect of soil, fertility and rhizospheric status on amorphous ferri-alumino silicate (AFAS) and total oxide (TOX) in non-colloidal clay

Fertility status	Alfisols		Inceptisols		Vertisols		Mean
	NR	R	NR	R	NR	R	
AFAS (%)							
Depleted	7.54	9.36	6.64	7.25	12.87	10.64	9.05^A
Original	8.23	7.47	6.00	5.68	12.25	10.53	8.36^B
Fertilized	8.24	7.76	6.26	6.26	11.32	10.20	8.34^B
Mean	8.00^C	8.20^C	6.30^D	6.40^D	12.14^A	10.46^B	
	8.10^B		6.35^C		11.30^A		

LSD (*P* = 0.05), S × F × R = 0.49

TOX (%)							
Depleted	1.73	2.07	2.48	2.93	3.05	2.89	2.52^A
Original	1.82	1.48	2.92	2.43	2.79	2.90	2.39^{AB}
Fertilized	1.55	1.64	2.98	2.42	2.33	2.70	2.27^B
Mean	1.70^C	1.73^C	2.80^{AB}	2.59^B	2.72^{AB}	2.83^A	
	1.72^B		2.69^A		2.78^A		

LSD (*P* = 0.05), S × F × R = 0.38

Means followed by the same letter within a row or column are not significantly different at 0.05 level of probability by the *LSD* range test. R – rhizosphere; NR – non-rhizosphere; S – soil; F – fertility status; R – rhizospheric status

ity status, Vertisols, and rhizosphere (Figure 1d). OBFE was formed in maximum quantity under rhizosphere (Figure 1e).

Chemical analysis of non-colloidal clay. Mean AFAS was significantly higher in depleted fertility status and Vertisols. Amongst interactions AFAS in Vertisols × depleted × non-rhizosphere was significantly highest (Table 2). TOX was highest in depleted fertility status and Vertisols, which was at par with Inceptisols. Mean TOX formation was statistically similar over rhizospheric status. Among different combinations of rhizosphere and fertility status, depleted rhizosphere possessed the maximum amount (Table 2). Depleted Vertisols contained maximum amount of OEAI in both rhizospheric and non rhizospheric condition. The effect was non-significant between rhizosphere and non-rhizosphere (Figure 2a). CRFE was significantly higher in Alfisols (3–5 times higher than Inceptisols and Vertisols). Depleted and fertilized fertility status contained higher mean CRFE under non-rhizosphere (Figure 2b). POFE was significantly higher in Alfisols than Vertisols and Inceptisols; and non-rhizosphere than rhizosphere. No significant difference, however, was observed when fertility status was compared (Figure 2c).

The rhizosphere possessed more OBAL and OBFE than non-rhizosphere (Figures 3d,e).

Fourier transform infrared (FTIR) spectroscopy. SRO minerals contain Al-OH, Si-OH and Fe-OH groups which are also common for other soil minerals. It is, therefore, not so easy to quantify the content through FTIR. The transmittance (%) in the samples with clay humus complex was higher, reduced when oxides and organic matter were removed and again increased when oxides, organic matter and SROs were removed (Figure 3). The FTIR spectra showed the adsorption maximum for Si-O-Si or Si-O-Al or Si-O-Fe stretching vibration ranged between 987–999/cm. Changes in intensity and positions of band were observed at 3400–3600/cm region particularly in Vertisols (Figures 3d–f). This region was also responsive to the size fraction of clay (not shown), as evidenced by the result obtained in non-colloidal clay, where this band was either absent or weak. There was no significant shift in FTIR peak over rhizosphere and non-rhizosphere in all of the soils. In the region of Si-O stretching vibration (1000/cm) in SRO removed samples; small peaks were observed (Figures 3c,f). Two absorption maxima at 2335/cm and 2366/cm in humus free colloidal
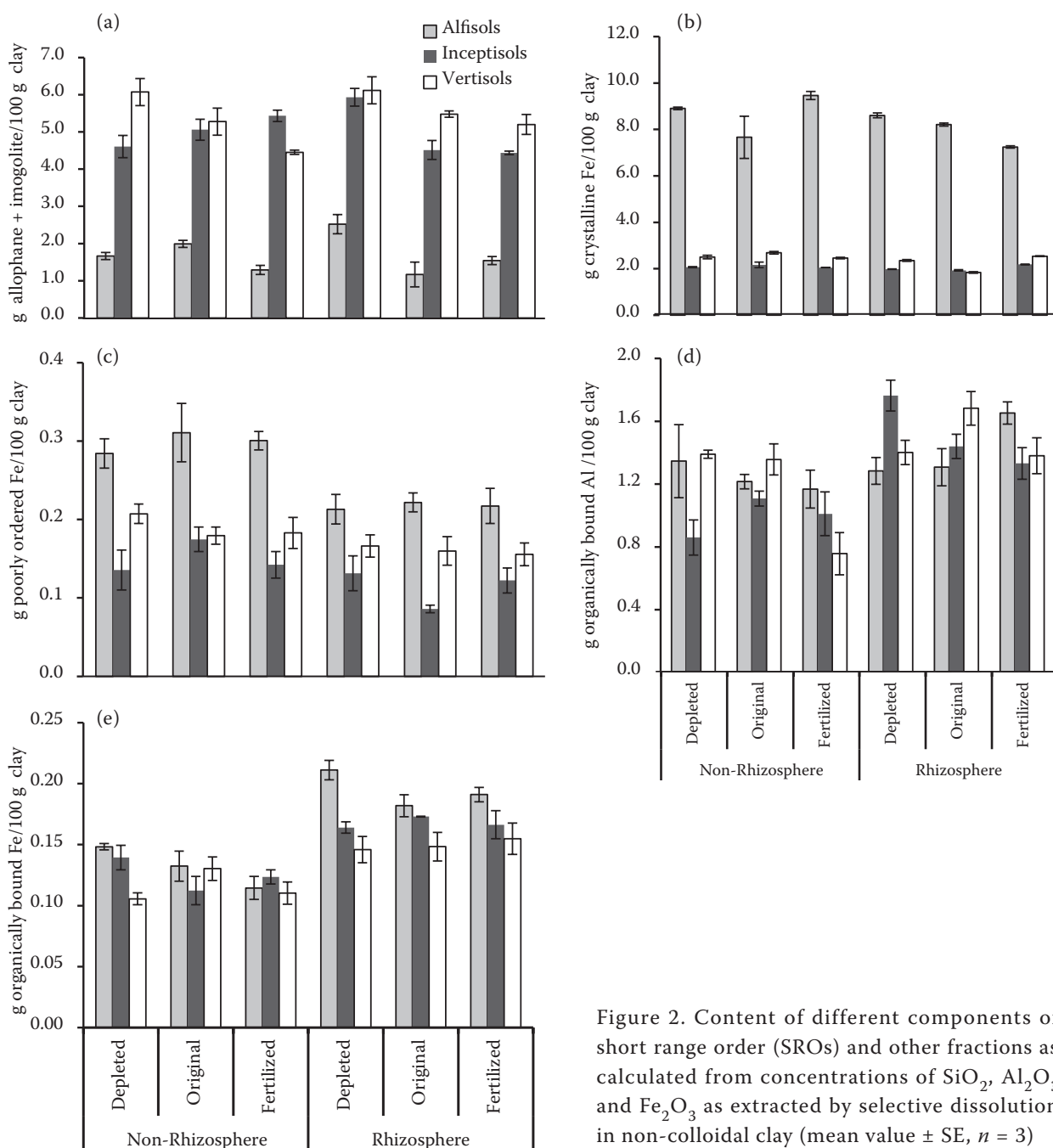
Figure 2. Content of different components of short range order (SROs) and other fractions as calculated from concentrations of SiO_2, Al_2O_3 and Fe_2O_3 as extracted by selective dissolution in non-colloidal clay (mean value ± SE, $n = 3$)

clay fraction of Vertisols is absent when SROs are removed by selective dissolution with 0.5 mol/L NaOH (Figures 3e,f).

DISCUSSION

The secreted LMWOAs facilitate breakdown of clay lattice partially (Datta et al. 2009) through chelation and simultaneously do not allow the oxides of Si, Al and Fe to combine to form crystal-line layer silicates, since recrystallization requires proton exclusion which is impossible under proton rich (acid) environment (Lou and Huang 1989). Non crystalinity thus, increased as reflected by increase in AFAS in rhizosphere after growing crops. Except the soil, the effect of other management factors viz. fertility and rhizospheric status showed opposite trend while measuring SROs in terms of TOX and OEAI. This may be due to the variation in the strength of the extractants. Boiling NaOH method was employed for
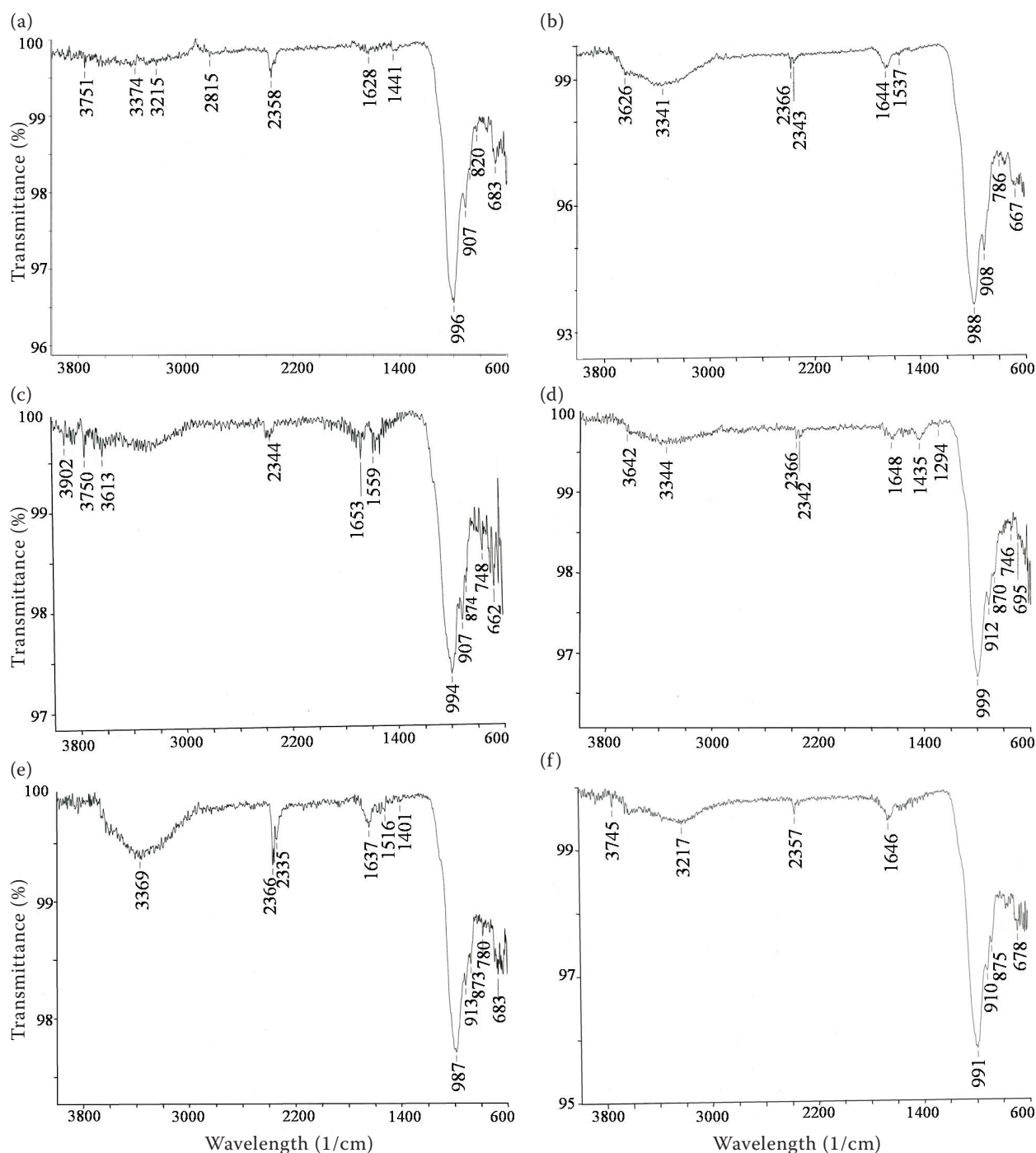
Figure 3. Fourier transform infra red (FTIR) spectra of clays from depleted rhizosphere (a) Inceptisols – colloidal clay-humus complex; (b) Inceptisols – humus free colloidal clay; (c) Inceptisols – humus and short range order (SRO) minerals free colloidal clay; (d) Vertisols – colloidal clay-humus complex; (e) Vertisols – humus free colloidal clay, and (f) Vertisols – humus and SRO minerals free colloidal clay

computation of AFAS, whereas mild extractant oxalate was used for TOX and OEAI. Oxalate predominantly extracts from organic complexes and SRO Fe-oxyhydroxides (e.g. ferrihydrite) and aluminosilicates (e.g. allophane and imogolite). However, imogolite is not completely dissolved

in only one treatment and phyllosilicates are only very slightly attacked (Pansu and Gautheyrou 2006). On the contrary, boiling NaOH treatment dissolved AFAS completely (Krishna Murti et al. 1976). Ferrihydrite, CRFE and POFE were highest in Alfisols in both the fractions, since such

soils were formed from Fe-rich parent materials. More OEAI formation in Inceptisols colloidal clay may be justified by high mica content (data not shown), which is more vulnerable to LMWOAs attack due to its high layer charge [Mica (0.7–1) > vermiculite (0.6–0.8) > smectite (< 0.6)] (Robert 1973). Highest TOX and OEAI were recorded under depleted fertility status treatments suggesting that the influence of organic acids under depleted fertility status is more prominent on non-colloidal fractions and Vertisols. Increase in OBAL and OBFE in rhizosphere (of both fractions) may be due to chelated Fe and Al (Datta et al. 2009). The formation of AFAS and TOX followed the order Inceptisols > Vertisols > Alfisols in colloidal clay, whereas Vertisols ≥ Inceptisols > Alfisols for non-colloidal clay. Comparing colloidal and non-colloidal clay, former contained more AFAS than later, however, the difference in AFAS content between these two clays were lower in Vertisols. The TOX, on the contrary, was just opposite to AFAS when size fractions were compared. In the study of SRO, TOX as measured is considered to be more meaningful than AFAS (Fey and Le Roux 1977). Depleted fertility status resulted in higher TOX formation especially in non-colloidal clay of all soils, whereas, original fertility status with Inceptisols and Vertisols and fertilized fertility status with Vertisols, indicating the pivotal role of fertilization on differential formation of TOX under both clay size fractions (McGahan et al. 2003).

The position of the absorption maxima of the Si-O vibrations near 1000/cm relate to the degree of polymerization of silica tetrahedra. When only Si-O-Si bonds are present the absorption maximum appears at 1080/cm, but as the proportion of Si-O-A1 and/or Si-O-Fe bonds increases, the maximum reduces towards 900/cm (Carlson and Schwertmann 1981). At removal of SROs by 0.5 mol/L NaOH, this adsorption maximum shifted towards 900/cm indicating the SROs are rich in aluminum. The extend of this shift is not very high, which may be due to the predominance of crystalline layer silicates (Wada and Greenland 1970). Changes at 3400–3600/cm region in Vertisols are due to OH stretching vibration of adsorbed water in SROs (Wada 1989). The absorption band at 1628–1653/cm in all the treatments is due to the HOH bending vibration of absorbed water and COO⁻ bending vibration of LMWOAs released in rhizosphere (Inoue and Huang 1984). The peak at 1435–1441/cm

in colloidal clay-humus complex of Inceptisols and Vertisols may be due to bending vibration of ionic carboxylate group of humic materials and/or LMWOAs (Inoue and Huang 1984).

From the present investigation the following conclusions may be drawn: (a) SRO formation are promoted by maize rhizosphere, however, rhizospheric effect is not so prominent in non-colloidal fraction of the clay; (b) nutrient stress, in general, lead to higher formation of SRO minerals through partial breakdown of crystalline phyllosilicates; (c) SRO alumino-silicates are more prominent in Inceptisols and Vertisols, whereas SRO Fe compounds are higher in Alfisols, and (d) the finer the fraction of clays, the more association of SROs is expected therein.

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