Amorphous and Crystalline Titanium and Iron-Titanium Oxides in Synthetic Preparations, at near Ambient Conditions, and in Soil Clays

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Abstract: A series of mixed iron and titanium oxide coprecipitates ranging in composition between $0 < Ti/Ti + Fe < 1$ was synthesized and aged under varying conditions of pH, temperature and time in order to establish a working model for pedogenic titanium and titano-ferric oxides. X-ray powder diffraction (XRD), selective chemical dissolution, magnetic susceptibility, charge distribution and electron optical data indicate that the freshly prepared Fe-Ti oxides consist of an Fe-rich (Ti-ferrihydrite) phase ($Ti/Ti + Fe \leqslant 0.70$) having pH-dependent positive charge and a Ti-rich phase ($Ti/Ti + Fe \geqslant 0.7$) with permanent and pH dependent negative charge.

Synthetic Ti-ferrihydrite and amorphous TiO_2 were completely soluble in acid ammonium oxalate (2 hr extraction in the dark) whereas poorly crystalline anatase (width at half height, WHH > 2.0° 2θ) was partly oxalate soluble. NH_4-oxalate soluble Ti was particularly high in soils developed under a cool montane climate (afro-alpine) and lower in soils of warmer subtropical climate, which contain anatase and rutile.

Several mixed Fe-Ti crystalline phases were identified after aging NH_3 coprecipitates of Fe and Ti nitrate at 70° C and pH 5.5 for 70 days: (1) goethite and hematite in the composition range $0 < Ti/Ti + Fe \leqslant 0.20$; at low Ti concentrations (<5 mole %) goethite was favored and/or hematite inhibited; (2) microcrystalline pseudorutile in the composition range $0.20 \leqslant Ti/Ti + Fe \leqslant 0.70$; (3) anatase and ferriferous anatase in the range $0.70 \leqslant Ti/Ti + Fe < 1.0$; with decreasing proportion of Ti the crystallinity of anatase decreased.

The results suggest that secondary or pedogenic Ti-Fe oxides can form by coprecipitation and crystallization in the weathering solution, and emphasize the essential role of water (as opposed to dry oxidation) in the alteration of primary titaniferous minerals.

Key Words: Anatase • Goethite • Hematite • Iron • Pseudorutile • Synthesis • Titanium

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