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Synthetic solid solutions between goethite and diaspore

CORRENS and von Engelhardt (1941) reported goethites containing aluminium in sedimentary ores. Similar observations were made by Schneiderhöhn (1964) and Schellmann (1964). Aluminium replaces iron in the goethite structure with diminution of the goethite unit cell constants. Norrish and Taylor (1961) consider that aluminium probably restricts the size to which the goethite crystals can grow; this could modify the phosphate-fixing power and other chemical properties of soil goethites. Furthermore, the aluminium content of goethites can be an important factor in bauxite ores. However, the mode of aluminium incorporation in goethites is not clear.

TABLE I. *AlOOH content of goethites prepared at various pH from 5 to 13. Time of ageing 6 months*

pH	Product*	AlOOH mol%	pH	Product*	AlOOH mol%
5	Goe.+gib.	15	10	Goe.+bay.	26
6	Goe.+gib.	18	11	Goe.+bay.	28
7	Goe.+bay.	22	12	Goe.+t.g.	33
8	Goe.+bay.	22	13	Goe.+t.g.	33
9	Goe.+bay.	26			

* Goe., goethite; gib., gibbsite; bay, bayerite; t.g., 'technical gibbsite'.

The following experimental investigations give new data for the formation of sedimentary goethites containing aluminium:

The precipitation of ferric hydroxide from 0·05 *N* iron(III) chloride solution with NaOH in the pH range 5 to 13 leads to goethite after a relatively short time of ageing. The precipitation from 0·05 *N* iron(II) chloride solution results in magnetite (Fe_3O_4) in the same pH range. However, the contemporaneous precipitation of iron and aluminium hydroxides from a 0·05 *N* Fe(II) chloride and a 0·05 *N* aluminiumchloride solution with NaOH at pH 5 to 13 forms, not magnetite, but goethite containing aluminium (Fe, Al)O(OH) (Table I). Increasing pH results in increasing Al content. Solid solution between goethite, α-FeO(OH), and diaspore, α-AlO(OH), is possible at 25 °C and 1 atm pressure in the range of 15 mol% AlO(OH) at pH 5 up to 33 mol% at pH 13.

The aluminium contents in goethites were determined by the change in the X-ray diffraction d_{111} (Correns and Thiel, 1963). Beside aluminium-containing goethites, gibbsite (γ-$Al(OH)_3$) is formed at low ph values, bayerite (α-$Al(OH)_3$) at neutral or alkaline pH, and the so-called 'technical gibbsite' (Franz, 1975) at strongly alkaline pH (Table I).

The contemporaneous precipitation of aluminium and iron(III) results in the formation of aluminium hydroxides together with aluminium-free hematite (Fe_2O_3).

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