

Low temperature transformation of schwertmannite to hematite with associated CO₂, SO and SO₂ evolution

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Abstract

Schwertmannite forms surface accumulations on organic litter in coastal flood plain acid sulfate soil landscapes of eastern Australia that are subject to wildfire and prescribed burning events. Naturally occurring schwertmannite (Fe₁₆O₁₆(OH)₁₂(SO₄)₂), is a product of acid sulfate soil oxidation and severe acidification. We report experimental evidence that relatively low temperature fires, fueled by organic-matter admixed with schwertmannite surface accumulations will transform the mineralogy of schwertmannite whilst liberating the Greenhouse gases CO₂, SO and SO₂. Three schwertmannite samples were examined, 2 natural and 1 synthetic. Thermal gravimetric analysis of the natural samples measured simultaneous CO₂, SO and SO₂ evolution at ~200-400°C. The natural schwertmannite, with organic matter, partially transformed to hematite in this temperature range. The synthetic schwertmannite, without organic matter, started to transform to hematite only at ≥600°C. The evolution of these gases and the partial transformation to hematite clearly shows combustion of organic matter, in close association with schwertmannite, raises the immediate temperatures to ≥600°C. When heated to ≥800°C all samples were completely transformed to hematite. This study provides the first evidence that wildfire can transform the mineralogy of schwertmannite at relatively low temperatures and therefore presents an original and significant insight into the iron cycle in coastal flood plain acid sulfate soil landscapes.

Key Words

Schwertmannite, acid sulfate soil, hematite, CO₂, SO, SO₂.

Introduction

Schwertmannite, an oxyhydroxysulphate of iron is a, poorly crystalline, yellowish-brown mineral with a structure analogous to akaganéite (Loan *et al.* 2004). Schwertmannite forms in low pH waters (2.8 to 4.5) of both natural waterbodies and waterbodies the result of mining and artificial drainage (Acero *et al.* 2006). Schwertmannite is a labile source of iron, sulfate and acidity and has a major role in controlling the geochemistry of acidified waterbodies (Burton *et al.* 2006). Sulfidic subsoils, deposited during the Holocene, underlay approximately 3 million hectares of Australian coastal flood plain. Coastal flood plain acid sulfate soils, disturbed and drained over the last 100 years, pose a land and waterbody management challenge (Johnston 2003). Schwertmannite forms surface accumulations in coastal flood plain acid sulfate soil landscapes of eastern Australia (Henderson *et al.* 2007). These accumulations have been implicated in maintaining severely acidic surface waters in these landscapes (Sullivan and Bush 2004) as well as being a primary iron mineral responsible for the formation of the monosulfidic black oozes accumulations (Burton *et al.* 2007; Henderson *et al.* 2006). Wildfire and prescribed fire regimes to reduce wildfire hazard frequently occur across the Australian continent including coastal flood plain acid sulfate soil landscapes (Bradstock *et al.* 2006). Such burning events can induce changes in iron mineralogy. For example, Grogan *et al.* 2003, attributed the transformation of goethite to maghemite in a coastal flood plain acid sulfate soil landscape to heating by bushfires of temperatures >300°C. An anomalous feature commonly observed in the wetland soils of these landscapes is the presence of abundant and thick (up to 5 cm) hematitic surficial layers, especially on soil profiles in areas affected by recent bushfires (Henderson *et al.* 2007). The presence or absence of reductants, including organic matter, elemental sulfur or sucrose, dictate the nature of the intermediate iron phases prior to complete conversion to hematite by heating (Loan *et al.* 2004). The transformation temperature is usually dependant on the crystallinity, and for iron minerals, the degree of aluminium substitution. The literature indicates that schwertmannite starts to transform to hematite at temperatures >600°C accompanied by evolution of SO₃ (Yu *et al.* 2002). Many of the studies into the behaviour of schwertmannite with heating were undertaken using purified or synthetic schwertmannite samples (Majzlan *et al.* 2004). The mineralogy including thermal behaviour of a purified schwertmannite sample from a naturally acidic stream has been reported to be essentially identical to that of synthetic samples (Schwertmann *et al.* 1995). However, natural schwertmannite accumulations in coastal flood plain

acid sulfate soil landscapes are usually in intimate association with appreciable quantities of organic debris such as leaf litter (Henderson *et al.* 2008). These organic materials are capable of ignition at relatively low temperatures ($< 400^{\circ}\text{C}$) (Dold *et al.* 2005) and accordingly may influence the thermal behaviour and subsequent mineralogy of natural schwertmannite accumulations from these landscapes. The objective of this study was to examine the influence of this closely associated organic matter on the thermal behaviour, mineralogy and evolution of gases during heating of natural schwertmannite accumulations from coastal flood plain acid sulfate soil landscapes.

Materials and methods

Natural samples were collected from coastal flood plains of New South Wales as leaf litter coated by schwertmannite. Samples were air dried and sieved. Synthetic schwertmannite was manufactured after Regenspurg (Regenspurg 2002). Samples were ramp heated in a muffle oven at $50^{\circ}\text{C h}^{-1}$ to both 400°C and 800°C . Randomly orientated powdered samples were examined using a Phillips PW 1050/70 diffractometer. Samples for X-ray diffraction analysis were gently hand ground. Total sulfur and carbon were analysed by an Elementar® combustion oven. Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Evolved Gas Analysis (EGA) were performed in a Netzsch STA 409C Simultaneous Thermal Analyser coupled to a Balzers Thermostar mass spectrometer.

Results

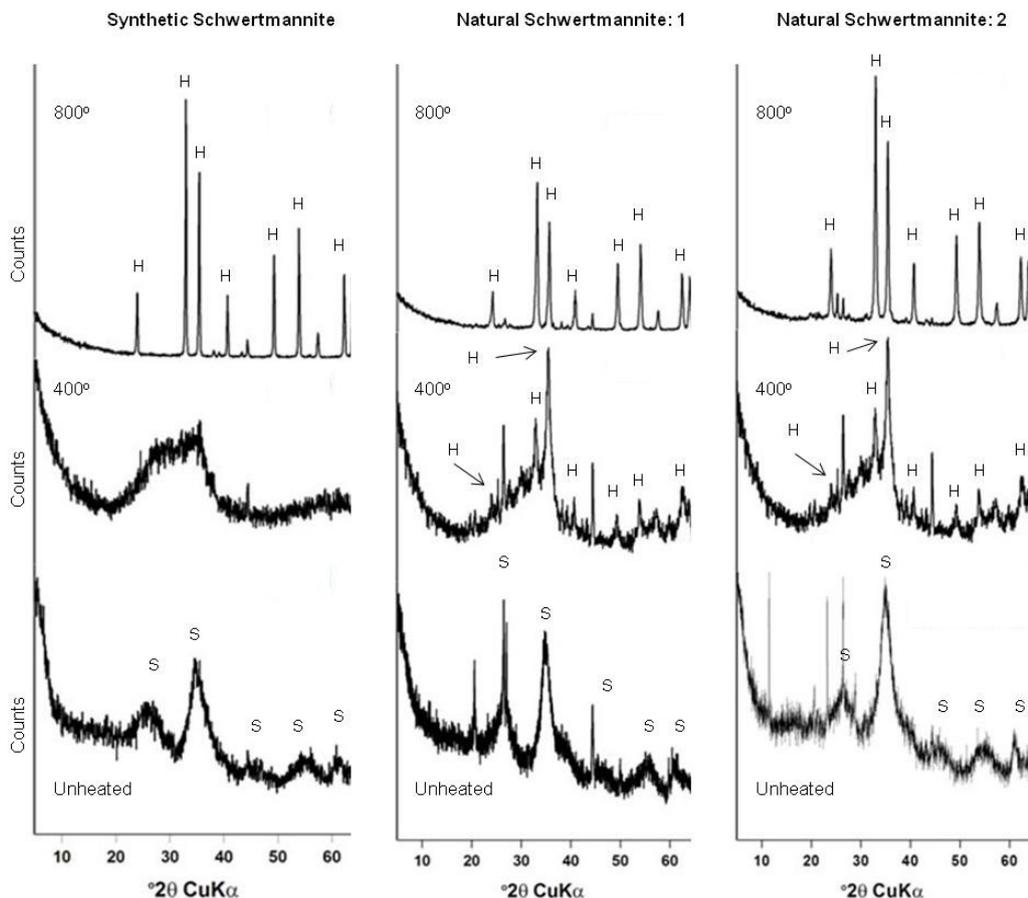


Figure 1. S = Schwertmannite Peaks and H = Hematite Peaks.

In line with the literature, heating to 800°C caused complete transformation of both natural and synthetic schwertmannite to hematite. However, heating to only 400°C caused partial transformation of the schwertmannite to hematite in the natural schwertmannitic accumulations but not in the synthetic schwertmannite.

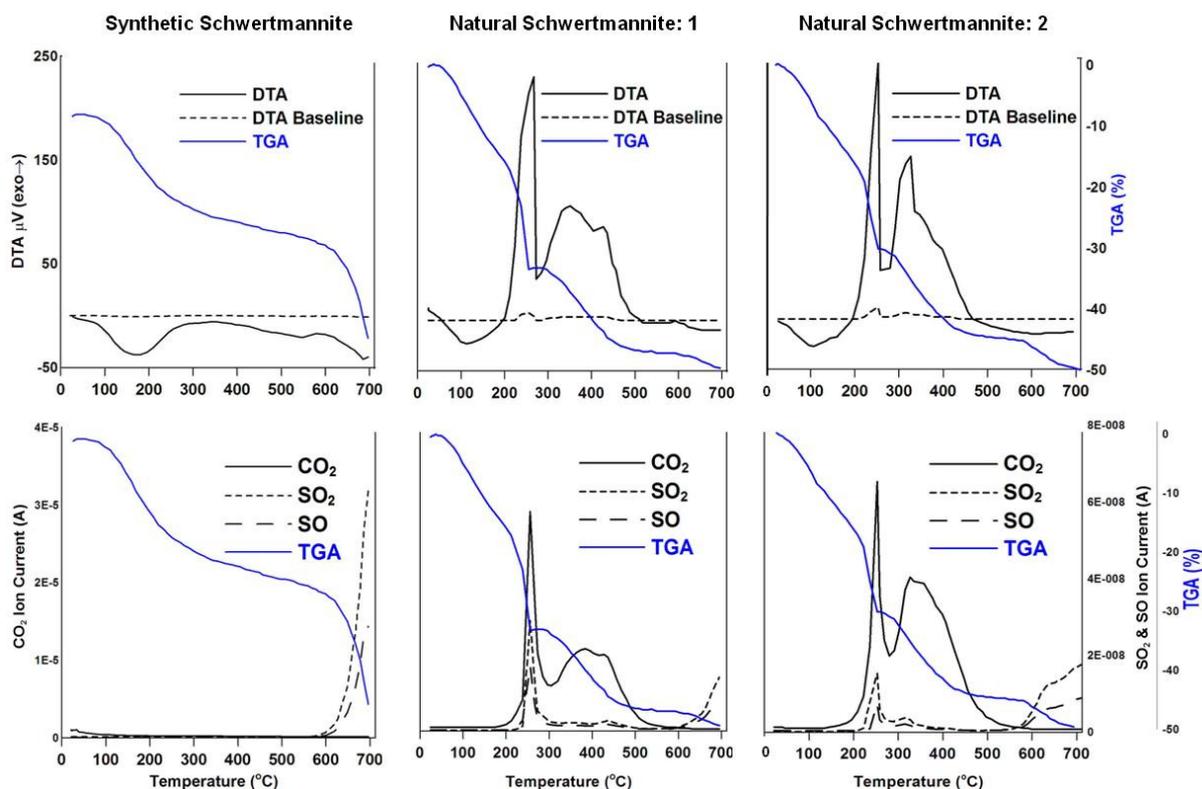


Figure 2. As all samples were heated, water was lost endothermically to ~200°C. After 600°C, SO and SO₂ was evolved, endothermically, as the synthetic schwertmannite began to convert to hematite. However the intimately admixed organic matter in the natural schwertmannite accumulations acted as an accelerant reacting exothermically from ~200 °C to 500°C causing the production of both heat and CO₂ upon pyrolysis. Micro-scale hot spots were created (>600°C) as evidenced by the production of SO and SO₂ (in accord with heat and CO₂ production), and appearance of hematite peaks at 400°C in XRDs.

Table 1. Heating to 800°C removed much of the sulfur but not all of it. Heating to 800°C effectively removed carbon.

Sample	Treatment	Sulfur Content (%)	Carbon Content (%)
Natural Schwertmannite: 1	Unheated	2.90	10.08
Natural Schwertmannite: 1	400°C	2.82	0.05
Natural Schwertmannite: 1	800°C	1.82	0.02
Natural Schwertmannite: 2	Unheated	3.17	12.91
Natural Schwertmannite: 2	400°C	3.05	0.05
Natural Schwertmannite: 2	800°C	0.72	0.02
Synthetic Schwertmannite	Unheated	7.41	0.06
Synthetic Schwertmannite	400°C	7.91	0.02
Synthetic Schwertmannite	800°C	0.02	0.01

Conclusion

This study has shown that the hematitic surficial horizons common in the soils of coastal flood plain acid sulfate soils landscapes can be readily formed by bush fires during dry seasons by the burning of organic matter-rich schwertmannite accumulations. Even low temperature (as measured conventionally) bush fires (e.g. < 300°C) could convert schwertmannite accumulations to hematitic surficial horizons due to the intimate association of the schwertmannite minerals with organic matter that acts as an accelerant. Bushfires in these landscapes can produce SO and SO₂ (in addition to CO₂) to the atmosphere during bushfires by the pyrolytic oxidation of iron precipitate minerals.

References

Acero P, Ayora C, Torrentó C, Nieto JM (2006) The behaviour of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. *Geochimica et Cosmochimica Acta* **70**, 4130-4139.

- Bradstock RA, Bedward M, Cohn JS (2006) The modelling effect of differing fire management strategies on the conifer *Calltris verrucosa* within semi-arid mallee vegetation in Australia. *Journal of applied ecology* **43**, 281-292.
- Burton ED, Bush RT, Sullivan LA (2006) Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica. Acta* **70**, 5455-5468.
- Burton ED, Bush RT, Sullivan LA, Mitchell DRG (2007) Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands. *Geochemical et Cosmochimica Acta* **71**, 4456-4473.
- Dold J, Greenberg B, Weber R, Zinoviev A, Sivashinsky G (2005) A porous-medium model for vegetation in bushfires. In '5th Asia-Pacific Conference on Combustion' pp. 289-292 Adelaide, Australia).
- Henderson SP, Sullivan LA, Bush RT, Burton ED (2006) The influence of naturally occurring schwertmannite on sulfur biomineralisation in coastal acid sulfate soils landscapes In '18th World Congress of Soil Science'. Philadelphia, USA.
- Henderson SP, Sullivan LA, Bush RT, Burton ED (2007) Schwertmannite transformation to hematite by heating: implications for pedogenesis, water quality and CO₂/SO₂ export in acid sulfate soil landscapes. In '17th Annual V.M. Goldschmidt Conference'. Koln, Germany (Geochemical Society, and European Society for Geochemistry).
- Henderson SP, Sullivan LA, Bush RT, Burton ED (2008) Thermal transformation of schwertmannite to hematite: anomalous stored acidity. In '6th International Acid Sulfate Soils Conference and the Acid Rock Drainage Symposium'. Guangzhou, Peoples Republic of China.
- Johnston SG, Slavich, P G, Hirst, P (2003) Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to *Melaleuca quinquenervia* encroachment. *Australian Journal of Soil Research* **41**, 1343-1367.
- Loan M, Cowley JM, Hart R, Parkinson GM (2004) Evidence on the structure of synthetic schwertmannite. *American Mineralogist* **89**, 1735-1742.
- Majzlan J, Navrotsky A, Schwertmann U (2004) Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite (~Fe(OH)₃), schwertmannite (~FeO(OH)_{3/4}(SO₄)_{1/8}) and ε-Fe₂O₃. *Geochemical et Cosmochimica Acta* **68**, 1049-1059.
- Regensburg S (2002) Characterisation of schwertmannite - geochemical interactions with arsenate and chromate and significance in sediments of lignite opencast lakes. University Bayreuth.
- Schwertmann U, Bigham J, M, , Murad E (1995) The first occurrence of schwertmannite in a natural stream environment. *European Journal of Mineralogy* **7**, 547-552.
- Sullivan LA, Bush RT (2004) Iron precipitate accumulations associated with waterways in drained coastal acid sulfate landscapes of eastern Australia. *Marine and Freshwater research* **55**, 727-736.
- Yu JY, Park M, Kim J (2002) Solubilities of synthetic schwertmannite and ferrihydrite. *Geochemical Journal* **36**, 119-132.