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Sideronatrite and metasideronatrite efflorescence formed in a coastal sea-spray environment

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ABSTRACT

Sideronatrite [$Na_2Fe(SO_4)_2(OH)\cdot3H_2O$] occurs as yellow botryoidal encrustations on low cliffs of weathered pyrite-bearing mudstones at Barton-on-Sea, Hampshire, England. Extensive areas of the cliffs, up to ~100 m^2, are coated with sideronatrite and its low solubility in cold water secures its longevity. Dry samples of sideronatrite convert readily to metasideronatrite [$Na_2Fe(SO_4)_2(OH)\cdot H_2O$], the reaction to sideronatrite being reversible. Sideronatrite, it is suggested, forms as a result of weathering of pyrite that is present in the argillaceous sediments and reaction with Na from the sea-salt spray.

KEYWORDS: sideronatrite, metasideronatrite, pyrite, weathering, efflorescence.

Introduction

WATER-SOLUBLE minerals, such as coquimbite [$Fe_2(SO_4)_3\cdot9H_2O$], tamarugite [$NaAl(SO_4)_2\cdot6H_2O$], and alunogen [$Al_2(SO_4)_3\cdot17H_2O$], which are normally associated with efflorescence in dry or arid environments, are reported as forming on rocks along the sea-shore (Hutton, 1970; Segnit, 1976; King, 1998). For example, the tamarugite described from a sea-shore environment is thought to have formed as a result of pyrite decomposition, which produced sulphuric acid that reacted with clays in the host shales and the Na from the sea spray (Segnit, 1976; King, 1998). Sideronatrite and metasideronatrite are found in arid regions together with other secondary sulphates (Bundy, 1938; Gaines *et al.*, 1997). Metasideronatrite was also reported on specimens that may have formed in a sea-spray environment (Ryback and Tandy, 1992), although few details were given. In addition, metasideronatrite and sideronatrite have been recorded from pyrite oxidation in coal fields (Randall and Jones, 1966; Zodrow *et al.*, 1979). In contrast, this paper reports on the formation of sideronatrite and metasideronatrite as a weathering product of pyrite-rich mudstones in a sea-shore environment.

Field relationships

A yellowish botryoidal crust is present on low cliffs of bluish to greyish argillaceous siltstones of the Upper Barton Beds, Upper Eocene, east of Barton-on-Sea (Burton, 1933). The beds belong to the H, I and J Horizons of the Upper Barton Beds. The yellow crusts are patchy and are present on areas ranging from a few cm^2 to ~100 m^2. When wet the colour of the encrustation is light yellow to orange-yellow, but when dry the colour lightens to whitish yellow to light yellow and exhibits a silky lustre. Thicker crusts have a dark brownish-orange coating. Individual crystals are not evident in hand specimen and under the optical microscope they appear as needles, typically 15 μm long and 1 μm wide and laths up to 25 μm long and 5 μm wide. Samples were collected on a rainy August day with strong onshore winds. As a consequence, the yellow crusts were constantly bathed in sea spray. Samples were collected and stored in their 'wet' state.

X-ray powder diffraction

X-ray powder diffraction patterns were acquired using a Rigaku D/Max-IIB diffractometer employing Cu-*K*α radiation. Attempts were made to make random powder mounts by packing the material into an Al holder but strong preferred orientation was still evident in the powder patterns. The powder pattern of the yellow material is complex with more than 70 reflections between 3 and 60°2θ Cu-*K*α. The pattern of the wet material shows reflections dominantly from sideronatrite, a few weak reflections of natrojarosite, and several weak unidentified reflections. No reflections of tamarugite are present. After drying in air, reflections of metasideronatrite are present. The intensities of the metasideronatrite reflections are dependent on the ambient relative humidity and its reflections dominate over those of sideronatrite on dry warm days. When heated to slightly higher temperatures, e.g. when placed in a sunny location, the sideronatrite changes completely to metasideronatrite in <1 h. In a damp atmosphere the metasideronatrite reverts to sideronatrite. The room temperature dehydration shown by the sideronatrite is in accordance with previous studies (Zodrow *et al.*, 1979), which showed formation of metasideronatrite from sideronatrite exposed to atmospheric conditions and when stored in a dry nitrogen atmosphere. Other studies (Scordari and Milella, 1982, Scordari *et al.*, 1982) heated sideronatrite from Sierra Gorda (Chile) at 130°C in order to obtain metasideronatrite. The ease with which metasideronatrite can rehydrate to sideronatrite was also noted by Césbron (1964).

Formation

Pyrite oxidizes in several stages under atmospheric conditions (Dent, 1986) to form sulphuric acid and iron hydroxide, possibly through the intervention of autotrophic bacteria such as *Thiobacillus ferrooxidans* (Banfield and Nealson, 1997). Reaction to form sideronatrite from pyrite in an oxidizing environment may be represented as:

$$FeS_2 + 2O_2 + 4H_2O + 2Na^+ \rightarrow Na_2Fe(SO_4)_2(OH)\cdot 3H_2O + H^+$$

With analogy to acid sulphate soils (Dent, 1986), this reaction probably proceeds through several stages of oxidation and the different stages do not necessarily occur at the same point. In acid sulphate soils there is spatial separation between pyrite and its oxidation products: jarosite, iron oxides, and gypsum (van Breemen, 1976).

The tamarugite that occurs in the sea-spray environments is thought to form by the reaction between sulphuric acid, from pyrite decomposition, and Al-rich clays in the sediments, and Na from the sea spray (Segnit, 1976; King, 1998). It is uncertain why the Barton-on-Sea efflorescence should be Fe-rich whereas minerals formed in nearly similar conditions are Al-rich. The presence of extensive covering of sideronatrite on cliffs at Barton-on-Sea may be attributed to its low solubility in cold water and hence it may survive for appreciable lengths of time.

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References

Banfield, J.F. and Nealson, K.H. eds (1997) *Geomicrobiology: Interactions between microbes and minerals*. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C., **35**, 448 pp.

Bundy, M.C. (1938) Mineralogy of three sulphate deposits of Northern Chile. *Amer. Mineral.*, **23**, 669–760.

Burton, E. St.J. (1933) Faunal horizons of the Barton Beds in Hampshire. *Proc. Geol. Soc. Lond.*, **44**, 131–67.

Césbron, F. (1964) Contribution à la minéralogie des sulfates de fer hydratés. *Bull. Soc. franç. Minéral. Crystallogr.*, **87**, 125–43.

Dent, D. (1986) Acid sulphate soils: a baseline for research and development. *International Institute for Land Reclamation and Improvement ILRI*, Publication **39**, Wageningen, The Netherlands.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B. and Rosenzweig, A. (1997) *Dana's New Mineralogy*, Eighth Edition. John Wiley & Sons, New York.

Hutton, C.O. (1970) Coquimbite from Nevis, West Indies. *Mineral. Mag.*, **37**, 939–41.

King, R.J. (1998) Tamarugite on the Isle of Wight, UK. *Mineral. Mag.*, **62**, 371–2.

Randall, B.A.O. and Jones, J.M. (1966) Sideronatrite from mineralized cavities in the Rising Sun colliery, Backworth, Northumberland. *Mineral. Mag.*, **35**, 983–90.

Ryback, G. and Tandy, P.C. (1992) Eigth supplementary list of British Isles minerals (English). *Mineral. Mag.*, **56**, 261–75.

Scordari, F. and Milella, G. (1982) Metasideronatrite: a mixture of coexisting compounds. *Neues Jahrb. Miner. Mh.*, 6, 255–64.

Scordari, F., Stasi, F. and Milella, G. (1982) Concerning metasideronatrite. *Neues. Jahrb. Miner. Mh.*, 8, 341–7.

Segnit, E.R. (1976) Tamarugite from Anglesea, Victoria, Australia. *Mineral. Mag.*, **40**, 642–4.

van Breemen, N. (1976) *Genesis and solution chemistry of acid sulphate soils in Thailand.* Pudoc, Wageningen, The Netherlands.

Zodrow, E.L., Wiltshire, J. and McCandlish, K. (1979) Hydrated sulfates in the Sydney coalfield of Cape Breton, Nova Scotia. II. Pyrite and its alteration products. *Canad. Mineral.*, **17**, 63–70.

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