Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Layer Structured Manganese Oxide Hydroxides
VI: Recrystallization of Synthetic Buserite and the Influence of Amorphous Silica and Ferric Hydroxide on its Nucleation*

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Abstract

Crystallinity and morphology of synthetic 10 Å-manganate (buserite) depend a) on the presence or absence of amorphous colloidal silica and co-precipitating amorphous ferric hydroxide, and b) on the ageing under pressure or normal conditions. Experiments have been carried out to age 10 Å-manganate at room temperature up to 14 years and to autoclave Ca-, Cu-, and Mg-buserite up to 200 hours at temperatures from 20 to 100 °C. Co-precipitation experiments have been carried out with amorphous silica and ferric hydroxide. Recrystallization leads to an ordering of the structure visible in additional reflections in the electron diffraction and to a crystal growth in one or, in twinned crystals, in two preferred directions. The presence of amorphous silica can entirely suppress 10 Å-manganate nucleation, and z-disordered manganate precipitates. Co-precipitating ferric hydroxide also suppresses 10 Å-manganate nucleation, while previously prepared ferric hydroxide has no influence. This explains the layered texture of deep-sea manganese nodules as an oscillating reaction controlled by depletion and enrichment of the aquatic phase in silica and ferric hydroxide.

1. Introduction

Na-10 Å-manganate (mineral name: Na-buserite) is the product of an oxygenation of freshly prepared $Mn(OH)_2$ in alkaline suspension under rapid O_2 saturation [1, 2]. The morphology of the resulting crystals has on occasions shown a slight growth along one or more preferred axes (depending on how crystals are twinned). We have therefore aged Na-buserite samples for 14 years in aqueous medium and exposed fresh samples to pressures of 200 atm (N_2 and air) at temperatures up to 75 °C in an autoclave.

10 Å-manganate is the dominant compound in manganese nodules rich in Cu, Ni, Zn and other metal ions. Its main characteristic is the exchange and incorporation of these ions into its lattice [3]. Manganese nodules with 10 Å-manganate exhibit a characteristic layered texture indicating an oscillating precipitation of 10 Å-manganate with intermittent precipitation of z-disordered manganate. It has recently been suggested by *Halbach* [4] that the pH depression following the precipitation of 10 Å-manganate may in turn precipitate amorphous silica which could inhibit further buserite formation until the solution is depleted sufficiently of SiO_2 such that buserite can again nucleate.

In order to investigate the influence of amorphous silica and to compare it with that of amorphous ferric hydroxide we have carried out series of preparations with these compounds.

2. Experimental

Buserite has been prepared according to *Wadsley* [1, 2]. Thoroughly washed samples were stored under H_2O bidist. at room temperature in 1966. For autoclave experiments, freshly prepared Na-buserite has been saturated with Cu^{2+}, Mg^{2+}, and Ca^{2+} as reported earlier [3, 5]. Ca. 7 g of the wet product were treated in an autoclave of 430 ml volume, in a covered Pt crucible filled with ca. 10 ml H_2O bidist., under air and N_2 (to increase pressure). The treatment with 200 atm at room temperature, 50, 75, and 100 °C, respectively, lasted up to 200 h.

For investigating the influence of silica and ferric hydroxide on buserite nucleation, the standard preparation [1, 2] has been used and to the Mn^{2+} solution were added immediately before precipitation with NaOH:

a) Amorphous silica (as LUDOX LS or HS, with negative surface charge; and LUDOX 130-m, with positive surface charge) to a final concentration of 0.001, 0.01, 0.1, 0.5 and 1-M (calculated as SiO_2).

b) Fe^{2+} (as $FeSO_4 \cdot 7H_2O$ p.a. MERCK) to a final concentration of 0.001, 0.01, 0.025, 0.05 and 0.1-M.

c) Separately prepared, fresh amorphous $FeOOH \cdot xH_2O$ in such amounts that the final suspension was 0.01, 0.02, 0.04, 0.08, 0.16, and 0.24-M (calculated as Fe^{3+} from the original amount of ferric nitrate). $FeOOH \cdot xH_2O$ was prepared after *Okamoto* [6]: 100 ml $Fe(NO_3)_3 \cdot 9H_2O$ (p.a. MERCK) 0.2-M were adjusted with 2-M HNO_3 to pH 1. This solution was dropwise added to 500 ml 10-M NaOH (p.a. MERCK) under vigorous stirring at room temperature. The precipitate was washed 5 times with 2 l portions of H_2O bidist. Aliquots of this suspension were subsequently used.

3. Results

3.1 Recrystallization of buserite

14 year old samples of Na-buserite show little indication of crystal growth, but autoclaved Cu-, M- and

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* Received Mai 19, 1980.

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Ca-buserite crystals grow along one preferred orientation into laths and fibres. The crystals, usually twinned or trillings, exhibit two or three sets of fibrous growth. X-ray diffraction shows a partial transition to 7 Å-manganate (depending on the temperature of the experiment) but most samples were intact in terms of X-ray diffraction. Single crystal electron diffraction patterns show more superstructure reflections and less streaking than in the initial product (fig. 1).

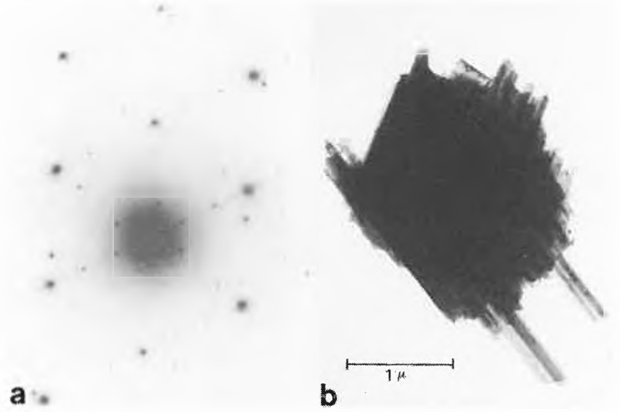

Fig. 1: Autoclaved Ca-buserite (8 h, 75 °C, 200 atm)
a) Selected area electron diffraction
b) Twinned crystal with laths growing out

3.2 *Nucleation of buserite in the presence of silica and FeOOH · xH₂O*

Fe^{2+} ions added immediately prior to oxygenation prevent entirely the nucleation of buserite at a concentration of 0.1-M. 0.05-M results in thinner platelets (broader X-ray lines); i. e. nucleation and growth of buserite are inhibited but not quite suppressed. (fig. 2). $FeOOH \cdot xH_2O$ *if prepared separately* has, however, up to 0.24-M no visible effect. Products, in this series, were mixtures of Na-buserite and amorphous ferric hydroxide.

Amorphous silica also inhibits nucleation of buserite, from 1-M with negatively charged silica particles, and from 0.5-M with positively charged silica (fig. 3).

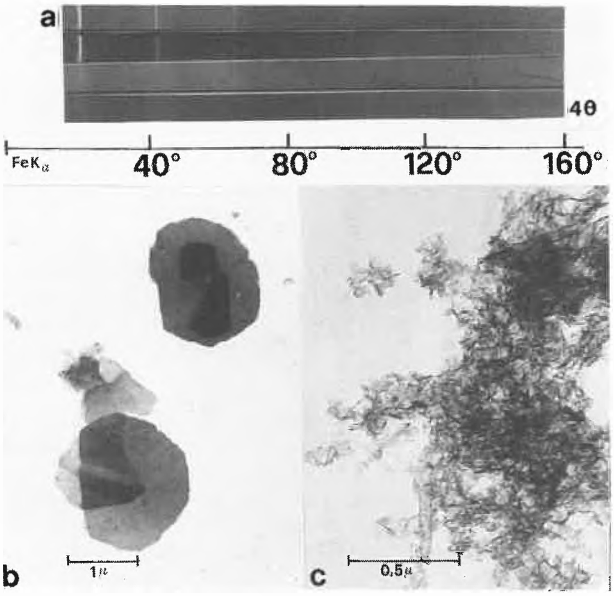

Fig. 2: Influence of co-precipitating $FeOOH \cdot xH_2O$ on buserite nucleation
a) X-ray powder patterns for $[Fe^{2+}]$ 0.001, 0.01, 0.05 and 0.1-M
b) Typical morphology up to 0.01-M $[Fe^{2+}]$
c) Product from $[Fe^{2+}]$ 0.05-M

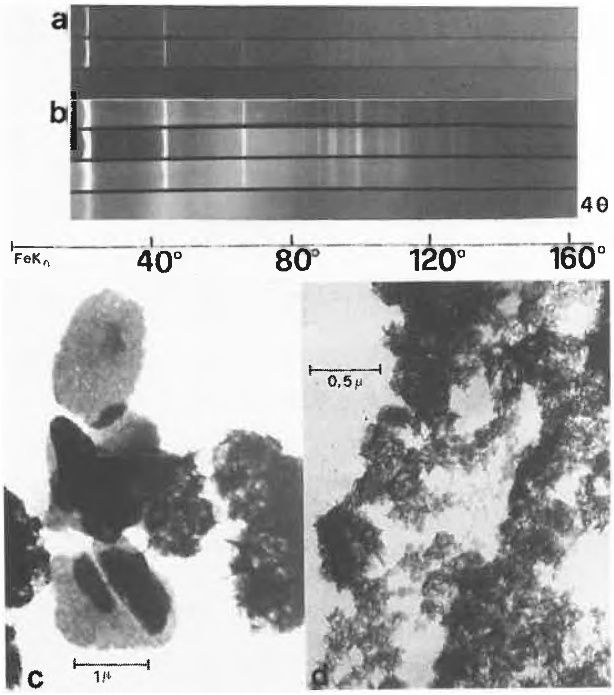

Fig. 3: Influence of colloidal silica on buserite nucleation
a) Silica with negative surface charge. X-ray diffraction patterns of products with 0.1, 0.5 and 1-M SiO_2
b) Silica with positive surface charge. X-ray patterns of products with 0.001, 0.005, 0.05 and 0.5-M SiO_2
c) Product with 0.5-M SiO_2 (positive surface charge). Buserite platelets still present
d) Product with 1-M SiO_2 (negative charge). z-disordered manganate intimately mixed with silica. Buserite formation is blocked

4. Discussion

Our results illustrate two influences: Buserite particles tend to grow with time, but their nucleation and growth may be suppressed under certain condidions. Higher pressures favour recrystallization; presence of amorphous silica inhibits nucleation. Co-precipitating ferric hydroxide also suppresses buserite formation but already existing ferric hydroxide has no influence. Recrystallisation is accompanied by structural rearrangement. If nucleation and growth are suppressed, z-disordered manganate forms and the well-known intimate mixtures of that manganate with silica and ferric hydroxide precipitate: These mixtures are the interlayer bands of low reflectance in manganese nodules, separating the high reflectance bands consisting of crystalline 10 Å-manganate.

This confirms the hypothesis of *Halbach* [4] that the oscillating precipitation of 10 Å-manganate and z-disordered manganate is caused by enrichment and depletion of the growth solution with silica and possibly other constituents. It also confirms that pore solutions (interstitial water) in the sediments furnish the material from which the layered manganese nodules grow.

The author is grateful to Miss *E. Ettinger* and Mrs. *Chr. Zahnd* for laboratory and other work, and to the Swiss National Fund for financial support.

Literature

1 *A. D. Wadsley:* J. Amer. Chem. Soc. *72* (1950) 1782.

2 *R. Giovanoli, E. Stähli* and *W. Feitknecht:* Helv. Chim. Acta *53* (1970) 209.

3 *R. Giovanoli* and *R. Brütsch:* Chimia *33* (1979) 372.

4 *P. Halbach* and *M. Özkara:* Geol. Rundschau *69* (1980) in press.

5 *R. Giovanoli, P. Bürki, M. Giuffredi* and *W. Stumm:* Chimia *29* (1975) 517.

6 *S. Okamoto, H. Sekizawa* and *S. I. Okamoto,* in: Reactivity of Solids. Proc. 7th IS RS Bristol July 1972. Chapman & Hall, London 1972, p. 341.