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Authigenic todorokite and phillipsite inside deep-sea manganese nodules

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Abstract

Phillipsite and todorokite assemblages are observed by scanning electron microscopy to line cavities and voids adjacent to areas where extensive leaching of biogenic siliceous debris has occurred inside deep-sea manganese nodules. Clusters of todorokite crystallites containing Ni and Cu also fill fissures, coat biogenic debris, and infill voids where biogenic debris once occurred in interiors of the nodules. We suggest that the post-depositional growth of phillipsite and conversion of δ-MnO_2 to todorokite inside manganese nodules is promoted by the dissolution of biogenic siliceous debris.

Introduction

Todorokite was shown by Frondel and others almost twenty years ago (Frondel *et al.*, 1960; Levinson, 1960; Straczek *et al.*, 1960) to be more widely distributed than indicated by its type locality in Japan (Yoshimura, 1934). Subsequently, todorokite, one of a score or more of manganese (IV) oxide minerals which have been documented (Burns and Burns, 1977a), was identified in marine manganese nodules (Hewett *et al.*, 1963), a potential ore deposit covering vast areas of the deep seafloor. Todorokite is generally regarded as the host phase for nickel and copper (Burns and Burns, 1977b), which are enriched in deep-sea manganese nodules by factors of 10^4 to 10^6 over their average abundances in seawater and in crustal rocks.

The authigenic zeolite phillipsite is also a common constituent of pelagic sediments. It is found in manganese nodules (Bonatti and Nayudu, 1965; Vassiliou and Blount, 1977), including the Ni–Cu-rich nodules from the north equatorial Pacific (Halbach *et al.*, 1975; Burns and Burns, 1978a,b). The coexistence of todorokite with authigenic phillipsite in these nodules suggests a paragenetic relationship between the two minerals.

Manganese nodule concretions comprise a complex assemblage of materials, including cryptocrystalline and X-ray amorphous hydrated oxides of Mn and Fe, crystallites of several detrital and authigenic minerals, hard-parts of marine organisms, fragments of fresh or altered basalt or basaltic glass (palagonite), *etc.* Such detritus appears to be essential for the nucleation and intimate intergrowth of hydrated Mn and Fe oxides (Burns and Burns, 1975), giving rise to the complex textures observed in polished sections of manganese nodules (Sorem and Fewkes, 1977). Despite the heterogeneity, cryptocrystallinity, and very fine particle sizes of the concretions, X-ray diffraction analysis has been the principal method for determining the mineralogy of manganese nodules (Burns and Burns, 1977a). Recently, the morphology and textures of crystallites in nodules have been observed by scanning electron microscopy (Sorem and Fewkes, 1977; Halbach *et al.*, 1975; Vassiliou and Blount, 1977; Burns and Burns, 1978a,b, and others), while transmission electron microscopy and selected area diffraction were used to identify individual phases in a seamount nodule (Heimendahl *et al.*, 1976; Fleischmann and Heimendahl, 1977). We have used scanning electron microscopy, in conjunction with X-ray diffraction and X-ray energy spectral analysis, to document evidence for diagenetic changes inside a suite of nodules from the north equatorial Pacific, and present results showing that todorokite and phillipsite have formed by post-depositional reactions involving amorphous or cryptocrystalline Mn(IV) oxides and detrital biogenic debris inside manganese nodules.

Experimental details

Nodules collected from several stations between 13°N 126°W and 10°N 153°W, within the area

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bounded by the Clarion and Clipperton Fracture Zones, were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray energy spectral (XES) analysis. Freshly-fractured nodule samples were mounted on aluminum stubs with silver paint and coated with an approximately 200A film of gold. Photographs were taken with Polaroid positive–negative PM-55 film on a Cambridge Stereoscan 2A operating at 20 kV. The semi-quantitative XES analyses used to determine the approximate compositions of the phases were made with a KEVEX 55 using Polaroid 107 film. Microsamples extracted from areas adjacent to surfaces examined by SEM were mounted in Debye-Scherrer cameras for XRD analysis, and exposed to Mn-filtered Fe*K*α radiation.

Mineralogy

The manganese oxide minerals most commonly reported in manganese nodules are todorokite, birnessite, and δ-MnO_2. In our suite of specimens only todorokite and δ-MnO_2 were positively identified in the XRD powder photographs of samples extracted from these deep-sea manganese nodules. Birnessite ("7A manganite") appears to be more common in nodules from seamounts and shallower seafloors. Todorokite, with a chemical formula approximating $(Ca,Na,Ba,Mn^{2+})_2Mn_5^{4+}O_{12}\cdot 3H_2O$ (Frondel *et al.*, 1960), is recognized as a constituent of manganese nodules by two diagnostic lines at 9.6A and 4.8A (Burns and Burns, 1977a). These lines also appear in XRD patterns of a synthetic sodium manganese(IV) oxide hydrate, the so-called "10A manganese" phase in early literature on manganese nodules (Buser and Grutter, 1956). This synthetic Na derivative was recently named buserite (Giovanoli *et al.*, 1971), and this name sometimes appears in European literature on manganese nodules. Some todorokites also give very weak lines around 7.0–7.3A, attributable to cryptomelane or hollandite impurities, or to birnessite which is a decomposition product of todorokite. In addition to the line at 7.08–7.27A, natural and synthetic birnessites also have a strong line at 3.5–3.6A, as well as at 2.46, 2.33, 2.03, and 1.71A (Glover, 1977). Thus the coexistence of the 7.08–7.27 and 3.5–3.6A lines are necessary to establish the presence of birnessite. Although many XRD powder photographs of the nodules used in the present study contain weak lines around 7.1A, these correlate with the absence of a line at 3.5–3.6A and with the presence of other weak lines at 4.99, 4.10, 3.76, and 3.24–3.1A, and occasionally at 6.37, 5.36, and 2.94 to 2.67A. These we attribute to the zeolite phillipsite $(K,Na,Ca)_2(Si,Al)_8O_{16}\cdot 6H_2O$. The XRD powder photographs of outermost surfaces of the nodules are generally featureless with considerable darkening of the films, suggesting that the microsamples contain phases amorphous to X-rays. Occasionally, broad diffuse lines centered around 2.40–2.45 and 1.40–1.42A are observed which are attributed to δ-MnO_2, a cryptocrystalline structurally-disordered derivative of birnessite. Although most nodules contain significant concentrations of Fe, the iron-bearing phases in most pelagic nodules also appear to be amorphous to X-rays. Recently, an iron-oxide phase in nodules was named ferroxyhyte and formulated as δ'-FeOOH, and suggested to be a disordered precursor to goethite, α-FeOOH (Chukhrov *et al.*, 1976).

Although the crystal structure of todorokite has not been completely determined, it is known that the structure accommodates divalent Mn, Mg, Ni, Cu, and Zn, and that these cations stabilize the phase (Burns and Burns, 1977a,b). Analyses of todorokites from a variety of parageneses, including ores (Straczek *et al.*, 1960; Frondel *et al.*, 1960), geodes (Finkelmann *et al.*, 1974), marine sediments (Dymond and Eklund, 1978), and manganese nodules (M. Siegel, unpublished results), indicate that Ca^{2+} is an essential constituent. Thus, during the present SEM study, todorokite was identified in manganese nodules by XES analysis on the basis of high Mn and moderate Ca contents. Identifiable Ni and Cu peaks, when present, were invariably associated with this phase.

Observations by scanning electron microscopy

The heterogeneity and cryptocrystallinity of manganese nodules makes them conducive to investigation by SEM. Towards nodule surfaces, a variety of biogenic debris and detritus may be seen (Figs. 1a–e). The biogenic debris in the nodules is composed of fragments of siliceous tests of radiolaria, diatoms, *etc.* but not calcareous tests, because the seafloor between the Clarion and Clipperton Fracture Zones is generally deeper than the carbonate compensation depth (at which $CaCO_3$ should be completely dissolved). The siliceous tests within a nodule, which occur in a matrix of δ-MnO_2, X-ray amorphous oxides of Fe, and aluminosilicates, can be seen to have undergone progressive dissolution in growth bands towards nodule interiors, giving a porous, leached texture in these zones (Figs. 1 and 2). Only larger, corroded siliceous spicules are found in areas beneath near-surface layers (Figs. 1e and 1f). Lining the walls of many of the cavities and voids in leached areas are euhedral crystals of phillipsite (Figs. 1e, 1f, and 2). The crystals are composite elongated prisms often showing penetration twinning. XES analyses proved these crystals to be potassium-rich (Burns and Burns, 1978b), which is a characteristic feature of phillipsites in pelagic sediments (Sheppard *et al.*, 1970). The delicate euhedral crystals and their proximity to leached biogenic debris (Figs. 1e and 1f) indicate that phillipsite grew *in situ* at the expense of the siliceous debris after the nodule was formed.

Some of the phillipsite crystals have inclusions of spherical clusters of crystallites of a Mn-oxide phase (Figs. 2a and 2b). More frequently, a finely crystalline meshwork has nucleated and grown on surfaces of phillipsite crystals, or at their base (Figs. 1f, 2a, 2d, and 2f). The XES analyses of these clusters (Burns and Burns, 1978b) show prominent Mn and Ca peaks as well as recognizable Ni and Cu peaks, identifying the mineral as todorokite. The meshwork of todorokite crystals also fills fissures (Figs. 3a and 3b), coats biogenic debris (Figs. 3c and 3d), and infills voids where biogenic debris once occurred (Figs. 3e and 3f). These delicate todorokite clusters are commonly enriched in Ni, Cu, and Zn relative to nearby growth bands.

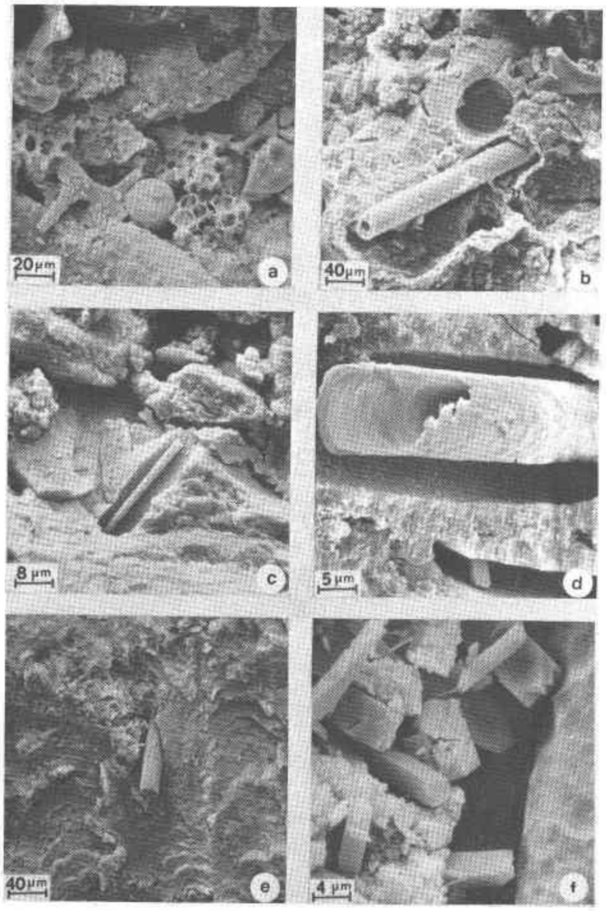

Fig. 1. Biogenic debris on or near surfaces of manganese nodules. The delicate fragments of siliceous tests observed on nodule surfaces (Fig. 1a) have undergone extensive dissolution beneath nodule surfaces (Figs. 1b–d), leaving only large, more resistant but corroded debris inside the nodules (Fig. 1e). Fig. 1f is an enlargement of Fig. 1e, and shows crystals of authigenic phillipsite and todorokite clusters adjacent to the corroded siliceous spicule.

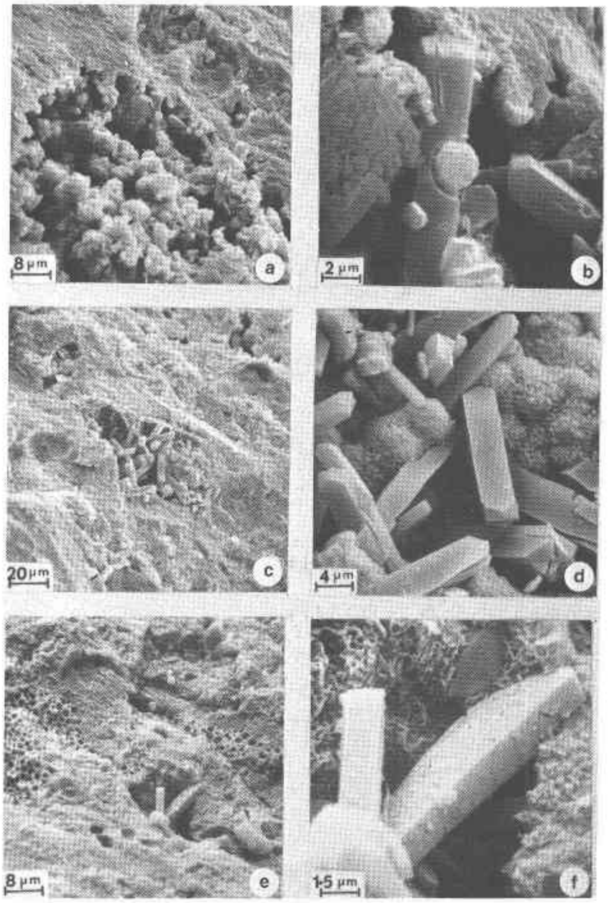

Fig. 2. Phillipsite crystals lining walls of cavities in areas where extensive leaching has occurred in nodule interiors.

Discussion

The origin of phillipsite in the marine environment has been the topic of considerable discussion ever since Murray and Renard (1884) reported this zeolite mineral in pelagic sediments. Phillipsite is now known to be an abundant constituent of surface sediments covering vast areas of the Pacific seafloor where sedimentation rates are low. The intimate association of phillipsite with pyroclastic material on the seafloor led to the suggestion that phillipsite forms as

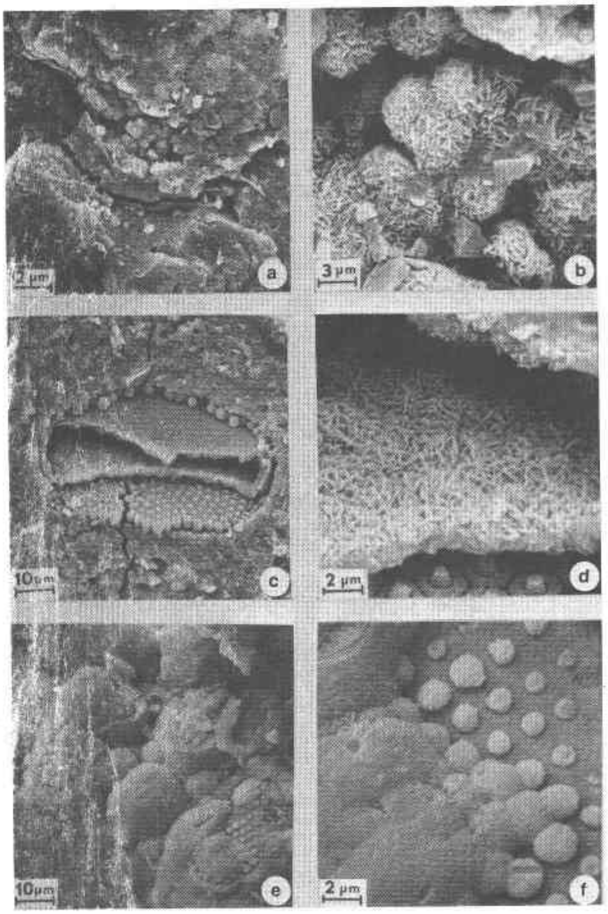

Fig. 3. Todorokite crystallites filling fissures (upper), coating biogenic debris (middle), and infilling voids where biogenic debris once occurred (lower).

a submarine alteration product of volcanic debris (Murray and Renard, 1884; Bonatti, 1965; Sheppard *et al.*, 1970). Bonatti observed the progressive development of phillipsite at the expense of palagonite associations in interiors and cores of manganese nodules (Bonatti and Nayudu, 1965). Recently, Vassiliou and Blount (1977) accounted for cavity crystals of phillipsite in nodules from the southern Argentine Basin as having formed from alteration of palagonite material.

Experimental studies (Hay, 1966) demonstrated that the formation of phillipsite is promoted by high silica activities, high alkali metal concentrations, and slightly alkaline pH. These factors are fulfilled by the leaching of volcanic glasses. Contact with seawater and pore waters in underlying sediments probably is essential for the formation of phillipsite on the seafloor. In their thermodynamic calculations of the stability of phillipsite in the deep sea, Glaccum and Boström (1976) noted that the relatively high silica content of bottom waters appears to be controlled by dissolution of siliceous tests from plankton, as well as the decomposition of volcanic glass. They suggested that phillipsite is formed by a reaction involving pelagic clays, opaline biogenic silica, and seawater containing dissolved alkali cations. This diagenetic reaction is consistent with our observations of the growth of authigenic phillipsite in manganese nodules.

The growth rates of phillipsites in marine sediments are slow (*e.g.*, 45 μm in 150,000 years; Czyscinski, 1973) and are comparable to the rates of accretion of manganese nodules (Ku, 1977). The phillipsites are commonly stained yellowish-brown by Fe-oxide inclusions (Sheppard *et al.*, 1970), indicating that this zeolite is an effective substrate for nucleating Fe(III) oxide hydroxides, which may also intergrow epitaxially with Mn(IV) oxides in manganese nodules (Burns and Burns, 1975). Our observations of the delicate meshwork of todorokite crystallites on or adjacent to authigenic phillipsite crystals in manganese nodules conform with models of nucleation and growth of manganese nodules, and of post-depositional metal enrichment processes described elsewhere (Burns and Brown, 1972; Greenslate, 1974; Burns and Burns, 1978a). In a study of micronodules from Pacific deep-sea sediments, Greenslate observed that embryo concretions nucleate within microcavities inside plankton skeletal remains and that the concretions are composed entirely of hydrated manganese oxides with negligible amounts of Fe, Ni, and Cu. He postulated that a similar process is responsible for the initial uptake of Mn onto the surface layers of large nodules. Our XRD and SEM measurements suggest that todorokite is formed when Mn(IV) oxide or Fe(III) oxide hydroxide oxidizes proteinaceous matter in biogenic siliceous debris (Burns and Burns, 1978a). The Fe^{2+} ions liberated in such redox reactions are re-oxidized by aerated seawater or Mn(IV) oxide to FeOOH, which coats phillipsite crystallites and forms a substrate for the deposition of todorokite. The biogenic siliceous matter is a possible source of Ni and Cu enriched in the manganese nodules in the north equatorial Pacific (Burns and Burns, 1978a). Boström *et al.* (1973, 1974) found that opaline silica derived from radiolarian tests, which constitute the siliceous oozes underlying these metalliferous nodules, is significantly enriched in Ni and Cu, possibly in the form of very stable organically-complexed Ni(II) and Cu(II) chelates (Burns and Burns, 1978a). We have suggested that, during dissolution of the biogenic silica in the sediments or inside the nodules, Ni^{2+} and Cu^{2+} ions are released when the organic chelates are oxidized by Mn(IV) oxide or FeOOH. These divalent transition-metal ions become available for uptake in a receptive host-mineral phase, such as contemporaneous authigenic todorokite formed from Mn(IV) oxide involved in redox reactions with biogenic matter.

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