

LETTERS OF THE COMMISSION ON MANGANESE (IAGOD)

REPORT ON THE TECHNICAL SESSIONS OF THE WORKING GROUP ON MANGANESE FORMATION, MONTREAL, CANADA

August 23 and 25, 1972.

JOHN VAN N. DORR II.
Vice-President

The Working Group for Manganese Formation (now the Commission on Manganese) held two sessions at which scientific papers were presented during the XXIV International Geological Congress at Montreal, Canada. In addition, after the business meeting on August 24, a 45 minute program on the exploration for, mining of, and extraction of metallic values from deepsea manganiferous nodules was presented by Messers. RAYMOND KAUFMAN and ROYAL HAGGERTY of Deepsea Venture, Inc. Attendance at the scientific sessions was over 50 persons at each session. The sessions were chaired by JOHN VAN N. DORR II, at the request of PROF. GYULA GRASSELLY, our President.

Twelve papers were scheduled but three authors were unable to attend the Congress and thus only 9 papers were presented.

On August 23, PROF. GRASSELLY of Attila József University, Szeged, Hungary presented the first paper, entitled *Thermal stability and oxidation of Mn_3O_4 in the presence of other manganese oxides*. The paper is printed elsewhere in this volume.

The second paper was presented by DRs. R. K. CORMICK, D. A. CRERAR, and H. L. BARNES of Pennsylvania State University USA, entitled *Geochemical controls on manganese distribution in amphibolite-grade metamorphic rocks*, and is printed elsewhere in this volume.

This paper was followed by a paper by PROF. RONALD K. SOREM of Washington State University, Pullman, Washington, USA, on *Mineral recognition and nomenclature in marine manganese nodules*. PROFESSOR SOREM's abstract follows:

In the literature of the past twenty years or more there is much confusion concerning the primary oxide minerals in marine manganese nodules. Most mineral identifications have been based upon X-ray diffraction powder data and have unfortunately been hampered by poor sampling, poor patterns, and non-uniform nomenclature. Difficulties have also arisen because of the lack of agreement on the nature and distribution of amorphous oxide material in nodules. The net result has been general lack of effective communication between many persons who have serious and similar interests in the problems of the character and origin of manganese nodules. It would appear that an attempt to set this mineralogical house in order is long overdue.

The following specific causes of confusion should be considered.

1. Most nodule samples used for X-ray diffraction have been impure mixtures.
2. Most X-ray samples have been altered by grinding.
3. Most nodule materials are poorly crystalline or amorphous and give diffuse X-ray patterns under even the best conditions.

4. Crystalline nodule materials have simple structures which permit ionic substitution, so *d*-spacings are somewhat variable for any one mineral.
5. Preferred orientation is common and affects X-ray patterns strongly.
6. The weak and diffuse X-ray patterns commonly obtained are difficult to compare with reference patterns published in tabular form.
7. Identification problems have led to erroneous nomenclature, where names for synthetic compounds (e.g., 10 Å -manganite) have been introduced for minerals (e.g. todorokite) already properly named.
8. Optical properties and textural relationships of minerals have been essentially ignored.

Four years of concentrated research on manganese nodules and the results of many years of mineralogical work on manganese ores prompt the following suggestions to improve the present situation.

1. Standard X-ray diffraction patterns of common supergene manganese minerals like birnessite, todorokite, rancieite, cryptomelane, and nsutite should be published and exchanged between research labs.
2. Standard X-ray samples should be chemically analyzed.
3. To avoid analysis of mixtures, all sampling for X-ray diffraction should be controlled by optical study of good quality polished sections.
4. All sampling of nodule materials for X-ray diffraction should be restricted to selective scratching or chipping of optically homogeneous areas. Grinding should be avoided to insure sharpest possible diffraction lines. Samples large enough for diffractometer slide mounts are rarely monomineralic and may show preferred orientation. The same problems occur in capillary tube samples. A thin fiber mount is best.
5. Electron probe analyses should be correlated wherever possible with optical data and should represent X-ray microsamples.
6. Valid new minerals, if they are found, should be properly characterized by X-ray, chemical, and optical data, and given names approved by nomenclature organizations.

It seems likely that most nodule mineralogical research is undertaken to aid in solving the general problems of nodule origin and history of growth. It is therefore suggested that wherever possible the data gathered be presented in a manner which will clearly show the relationship of the samples studied to the entire nodule under investigation. This can be done conveniently by using a photomicrograph of an entire nodule cross-section, preferably obtained with vertical illumination similar to that of the ore microscope, as a map on which data can be plotted.

DR. ALLAN R. FOSTER, also of Washington State University, then gave a paper on the *Growth history of manganese nodules from the Baja California Seamount Province*, the abstract of which follows:

Study of 46 manganese nodules collected from 9 separate dredge hauls 370 km southwest of Baja California, Mexico, has provided new insight into the processes controlling nodule formation. Detailed studies of polished nodule cross-sections, using ore microscopy, XRD, and XRF macroprobe techniques reveal intricate internal structures and systematic chemical and mineralogical variations.

Nodule growth is attributed to discontinuous accretion of thin, opaque, crystalline or X-ray amorphous shells about a central core (commonly a nodule frag-

ment). Crystalline laminae composed of intimate intergrowths of cryptocrystalline todorokite and birnessite are much less abundant than X-ray amorphous shells but are of special interest because they contain the greatest concentrations of Ni, Cu, and Mn. Textural and mineralogical evidence suggests a colloidal origin for both types of shell material.

Five distinctive textural patterns called zones are recognized in the sequences of shells. Zones are designated massive, mottled, compact, columnar, and laminated and differ in composition, texture and homogeneity. The massive and mottle zones contain the highest concentrations of Mn, Cu, Ni, and K, while the columnar, laminated and compact zones contain the greatest concentrations of Fe, Ti, Ca, and Si. The mottled and columnar zones are the most abundant.

Each zone type evidently forms during a period characterized by a relatively stable and unique sea-floor environment. Most nodules show a succession of zone types indicating that major environmental changes took place during growth. Minor textural differences between nodules suggests that local fluctuations in the depositional environment occurred. Environmental factors involved probably include fluctuations in Eh, pH, ion concentration of the sea-water and substrate pore water and the relationship of each nodule to the sea-floor sediment-water interface.

Ocean bottom photographs indicate that opposite sides of a nodule are exposed to different depositional environments; namely, the sea-floor sediment and the ocean bottom water. Textural evidence indicates that nodule growth occurs on both sides of the interface and that certain zone types are formed in each environment. Formation in contact with the sediment is suggested for the mottled, columnar and laminated zones. The massive and compact zones are thought to grow in the sea-water environment. For a given period of time, greatest thicknesses of nodule material appear to accumulate on the side of the nodule exposed to the sediment.

Many concentric growth shells appear to have undergone "diagenetic" changes after burial under succeeding layers. The "diagenetic" processes involved are:

1. filling of porespace with Mn—Fe-rich oxides.
2. replacement of clay and foreign inclusions by Mn—Fe-rich oxides.
3. minor replacement reactions between different species of opaque, X-ray amorphous materials.
4. replacement of fossil tests by todorokite and birnessite.
5. recrystallization of oxide material, especially in older portions of a nodule.

The rate and extent of these "diagenetic" changes is probably enhanced by the great porosity and permeability of the nodules.

Physical forces affect nodule development as well. Periodic overturn of nodules is indicated by zonal sequences displaying alternating zone types characteristic of different depositional environments. Movement may result from the activity of benthonic organisms, water or bottom movement, imbalance and toppling due to irregular growth, or other unknown forces. Abrupt interruptions of nodule growth, as recorded by nodule fragment cores, indicate past episodes of nodule shattering. Textural evidence suggests that internal forces cause nodule breakage.

This study of whole nodule textural and chemical relationships reveals that nodule formation is a much more complex process than most investigators have indicated. Discrete nodule growth shells, if treated as stratigraphic units, reveal

a detailed history of nodule growth. If present estimates of rate of nodule accretion are correct, the nodules studied display a record of environmental changes on or near the sea floor during the past several million years.

The final paper of the session was by DR. RONALD H. FEWKES, also of Washington State University, on *Conglomerate manganese nodules from the Drake Passage*, the abstract of which follows.

Marine manganese nodules from the Drake Passage area formed in an environment characterized by abundant terrestrially derived detritus. A textural study of twelve polished nodule sections reveals complex growth relationships between the detritus and the oxide minerals found in the nodules. Nodule growth can be attributed to the accumulation of clastic material, iron and manganese oxides, and microscopic fragment-rimmed pods.

The incorporation of detrital material in Drake Passage nodules is an important mechanism of growth. The size of the individual fragments varies, but it is estimated that at least 80 percent are less than 100 microns. The fraction less than 100 microns is composed of detrital quartz and feldspar with a scattering of other minerals and organic debris. The other 20 percent of the detrital material is made up of rounded rock fragments as large as one centimeter in diameter. Typical Drake Passage nodules consist of a rock core surrounded by accumulations of angular clastic debris, with a matrix or cement of iron and manganese oxides. The contact between the individual fragments and the oxides is sharp and distinct. Where several large rock fragments are found in the interior of the nodules, the oxides appear as distinct layers only on the side of the fragments away from the nodule core. Fragments on the outer edges of the nodules are generally enclosed by oxides, but many have prominent oxide accumulations on their exterior sides, with the thickest oxide layers concentrated around the sharpest points of the fragments. Where detrital material is minimal, oxide minerals occur in colloform layers which in some nodules form columnlike structures. These structures consist of alternating bright (highly reflecting) and dark laminae. The highly reflecting layers contain chiefly oxide minerals while the darker layers are detritusrich. Nodules with an abundance of detrital material or an abundance of microscopic fragment-rimmed pods have few well-developed columnar structures.

The microscopic pods found in the nodules are roughly circular in form and consist of a nucleus surrounded by angular clastic fragments. The nucleus is very fine-grained and non-opaque and has the appearance of clay. The surrounding fragments are detrital quartz or devitrified glass shards. Pod diameter is generally less than 200 microns. The origin of these pods remains a mystery but possible organic and inorganic modes of origin are suggested.

The textural features of Drake Passage nodules may be characteristic of nodule growth in an environment where abundant wind, water, and ice transported material is accumulating. The contrast with nodules of the open ocean where low sedimentation rates prevail is striking.

The first paper of the August 25 session was by DR. IGOR M. VARENTSOV of Geological Institute, Academy of Sciences, Moscow, USSR, our Secretary, and N. V. PRONINA of the same Institution. The result of experiments on *The study of sorption by natural iron-manganese oxides from seawater in the presence of complex-forming compounds* was reported.

Highly selective sorption of Ni and Co was observed. In the runs with biogenic

forms of these metals, after 20 days as much as 77.8 percent Ni was removed from the seawater and complete extraction of Co took place. The range of concentration of these metals in solution was 10 to 100 ppb. The character of isotherms of the Ni and Co sorption from seawater in the presence of complex-forming agents citric acid give evidence that, even at the high amounts of sorbed metals (10 to 40 weight percent), there is no tendency for reaching the limits of sorption capacity.

The experiments on desorption showed that the initial stages of the process are of ion-exchange character, mainly for Ni, to a lesser extent for Co. In the later stages, the formation of nonexchangeable, firmly fixed forms of Co and Ni takes place. These forms are hydroxides of Ni and Co. Chemosorption plays the leading role, with an autocatalytic oxidation process of accumulation of these metals. The newly formed phases act in the future cycles of interactions as active sorbents.

This paper was followed by one by DR. D. A. CRERAR, R. K. CORMICK, and H. L. BARNES of Pennsylvania State University, USA, on *Organic controls on the sedimentary geochemistry of manganese*, printed elsewhere in this volume.

An interesting newly discovered and very large deposit of manganese carbonate in Mexico, the *Molango manganese deposit, Hidalgo, Mexico*, was described by INGS. E. TAVERA and R. ALEXANDRI, with ING. ALEXANDRI delivering the paper.

These manganese deposits are in the Upper Jurassic Taman formation, and the manganese limestone ranges from 5 to 30 percent Mn over a thickness of about 25 meters, with the higher values concentrated in a range of 5 to 10 meters near the base of the unit. The manganese limestone has been traced in outcrop over an area some 50 km in north-south extension and 25 km in east-west direction. It is included in a thick sequence of Lower Permian and Mesozoic sedimentary rocks that unconformably overlies a Precambrian metamorphic complex and is unconformably overlain by Tertiary basalts. The area is in the southern part of the Sierra Madre Oriental and occurs within one of the major anticlinal structures of that range.

The syngenetic manganese deposits are primary manganese carbonates amenable to calcination, producing a clinker containing over 40 percent Mn. The manganese occurs as kutnahorite and rhodochrosite, which are distributed in thin bands rhythmically distributed in the manganese unit. Pyrite and organic carbon also are found in this portion of the Taman Formation, as well as clay bands. The manganese was deposited in a transgressive and strongly reducing marine environment.

It has been calculated that, although at least half the manganese zone of the Taman Formation has been removed by erosion, the remaining part contains about 1,350 million tons of manganese metal. Much of this is in rock now too low grade to be economically extractable, but the concentration of manganese is, from a geologic viewpoint, noteworthy. No apparent source for this quantity of manganese is now known and it must be presumed that the metal was derived by the weathering of continental rocks and transported to the depositional area by surface waters. No contemporary volcanic action in the region, either submarine or terrestrial, is known.

Epigenetic deposits of manganese oxide, some of battery grade, were formed by weathering of the syngenetic carbonate and are also being exploited. Owing to

the extreme relief in the area and the consequent rapid erosion, these are small and pockety, being controlled by topographic and structural features which permitted local accumulation of the weathering products.

The final paper on the scientific program was *Manganese deposits of South Korea*, presented by PROF. SOO JIN KIM. The paper is printed elsewhere in this volume.

REPORT ON THE BUSINESS MEETING OF THE WORKING GROUP
ON MANGANESE FORMATION (NOW COMMISSION ON MANGANESE)

August 24, Montreal, Canada

DR. JOHN VAN N. DORR II
Vice-President

DR. I. M. VARENTSOV
Secretary

PROF. DR. GY. GRASSELLY
President

The technical session and a business meeting of the Working Group on Manganese Formation were held in conjunction with the XXIV International Geological Congress. The business session was held August 24 and was followed by a 45 minute presentation on prospecting for and exploiting deep sea manganese nodules by officers of Deepsea Ventures, Inc. The technical sessions and the business meeting were chaired by Vice-President DR. JOHN VAN N. DORR II at the request of PROF. GRASSELLY and were attended by more than 50 geologists. About 20 persons attended the business meeting.

The business meeting was addressed by PROF. GRASSELLY, President, on the history of the WGMF. DR. VARENTSOV, Secretary, discussed results of past activity and the present situation of the WGMF. Both emphasized the necessity for fuller cooperation from country representatives and for fuller representation from the rest of the world.

Till now the following countries are represented in the WGMF: Bulgaria, Czechoslovakia, Hungary, India, Japan, Korea, Romania, Soviet Union, United Arab Republic, United States of America, Yugoslavia. DR. LOUIS DOYEN of Belgium (Louis Doyen, Licencié en Sciences Géologiques et Minéralogiques, Assistant à l'Université, 14—18, Rue des Pavots, Bruxelles 3, Belgium), DR. HUBERT PÉLISSONNIER (Professeur à l'École des Mines, 60 Boulevard Saint-Michel, Paris VI, France), PROF. EVARISTO RIBEIRO FILHO (Geologo, Professor Livre Docente, Instituto de Geociências, Universidade de São Paulo, Depto. de Geologia Econômica, Rua Iraci, 590, 01457, São Paulo, Brazil) agreed to serve as national representatives for their countries. DR. HANSJUST W. WALTHER, Wissenschaftlicher Direktor in der Bundesanstalt für Bodenforschung (3 Hannover-Buchholz, Alfred-Bentz-Haus, FRG) and ING. GEOL. RAFAEL ALEXANDRI R. (Sociedad Exploradora Minera, S. A. de C. V., Viena 4, 3^{er} piso, Mexico 6, D. F., Mexico) promised that in the near future they will give personal proposals for representation of the Federal Republic Germany and Mexico, respectively. Naturally, it would be successful to have national representatives for Australia, Cuba, China, Ghana, Indonesia, Morocco, Pakistan, South Africa, too. The WGMF will request the Geological Surveys of these countries to propose proper experts to fulfill this duty.

A change in the name and status of the Working Group on Manganese Formation to Commission on Manganese was proposed and approved. The Council of IAGOD was requested to approve this change, which was done on August 25.

The next technical sessions and business meeting of the Commission on Manganese will be held during the IAGOD Symposium in Varna, Bulgaria, in 1974 and the dates September 19—21 were selected. About 20 technical papers are hoped for in the first and last of these dates and the agenda for the business meeting on September 20 was discussed and approved. The agenda of the business meeting: a) Report on the activity of the Commission on Manganese; b) Preparation of the International Symposium on Manganese at the XXV IGC, 1976, Australia and discussion of the progress made in the last two years; c) Election of officers of the Commission on Manganese for four-year period according to the IAGOD Statutes.

The Commission on Manganese (former Working Group on Manganese Formation), an affiliate of IAGOD, has as its purpose the promotion of international cooperation in advancing knowledge of this essential element to our civilization. To this end, *it is proposed that a symposium be organized as part of the XXV International Geological Congress to be held in 1976.*

The proposed symposium will try to assemble in one publication our present knowledge on the geochemistry, mineralogy, geologic associations, occurrence, and distribution of manganese in earth's crust and oceans. During the last two decades, powerful new tools have extended scientific knowledge of the habits of manganese, great new deposits have been found and developed, much new and important information has been secured on previously known deposits, the potential of the sea floor nodules recognized. An updating of the excellent Symposium on Manganese held at the XX IGC in Mexico, 1956, will be of great benefit to the profession and to society. The symposium hopes to illuminate the relation between scientific investigation and practical development.

The general organization of the XX IGC Symposium would be followed. General papers, as outlined below, will be invited on the broader aspects of manganese geology, investigation, and resources. Individual countries, through their Geological Surveys or other appropriate agencies, will be invited to contribute papers on the occurrence and resources of manganese within their borders. These will be grouped by continents and, if appropriate, a summary by continents prepared. *At the Congress itself, the general papers will be presented; there would not be time for presentation of all the detailed papers on individual countries. These, with the general papers, would be published in a multivolume monograph, in English.*

The proposed general organization of the symposium is as follows:

I GENERAL PROBLEMS

- a) Classification of manganese deposits
- b) Patterns of distribution of manganese in the earth's crust in space and time. Relation to tectonic plates
- c) Problems of manganese mineralogy
- d) Problems of manganese geochemistry
- e) Manganese ore deposition in recent basins
- f) Microbiological aspects of manganese ore deposition
- g) Problems of beneficiation of manganese ores

II PHYSICAL AND CHEMICAL METHODS OF INVESTIGATION OF MANGANESE ORES

Review of modern methods of chemical and physical analysis of solids as applied to manganese ores

III GEOLOGY OF MANGANESE DEPOSITS

- a) Western Hemisphere
- b) Africa.
- c) Europe, including the USSR
- d) Asia
- e) Australia and Oceania
- f) Ocean basins, lakes, and mediterranean seas

In order to give coherence to the papers on the manganese deposits in individual countries, the following outline is suggested to contributors to Section III.

1. Name, geographical and climatological relations, short statement on general geology as significant to manganese deposition.
2. History of production, with grade and tonnage broken down, if appropriate, by districts and major deposits.
3. Types of deposits represented in the country, with relative importance, grades, and productivity.
4. Geology of major deposits or districts, with particular attention to primary, metamorphic, and supergene mineralogy; structural and stratigraphic relations; wall rocks and wall rock alteration, age, and metamorphic grade; analyses of ores and protore and wall rocks, including minor and trace elements; ore controls; present and, if known, past climatic regimes; physiographic setting; depth and effects of weathering and supergene action; environment of sedimentation (if sedimentary), deduced temperature environment and associated metals (if hydrothermal), nature of and relations with associated volcanic rocks (if volcanogene); relations, if any, with iron-formation; sources of manganese in the deposits. (Geologic maps and sections as appropriate.)
5. Reserves, with estimated tonnage and grade in as much detail as seems appropriate. Identified resources.
6. Possibility of undiscovered reserves and resources.
7. Mining and beneficiation methods used (short and general).
8. Special problems relating to manganese mining in the country.

Most of the papers on individual countries could be short and succinct because few countries possess large reserves of manganese ores. In the case of countries such as Australia, the USSR, South Africa, Brazil and some others with very large or newly developed reserves, more extended papers would be justified and needed. Emphasis on new information and facts would be requested, with special attention to possibilities opened by modern technology in transport, beneficiation, and mining.

The Symposium on Manganese published by the XX IGC in 1956 consisted of five volumes totaling about 1600 pages. This was large type and small pages. Using smaller type and perhaps larger pages, the proposed publication might involve approximate the same number of pages or possibly a relative small percentage more.

We hope that all countries interested in manganese research will contribute. The focus of the IIIrd section of the symposium should be on new information.

Concerning *the preparation of the monograph* on manganese on a world-wide basis, with the suggested structure, among myriad others, two principal problems are now paramount: 1) to identify an active group of contributors to cover the indicated subjects; 2) to secure backing for the publication of such a large enterprise.

The effectively attack problem 1, the cooperation not only of individuals but of Governmental, University, and private organizations throughout the world will be essential. Various suggestions, many very constructive, were made to solve problem 2, but no decisions were reached. These suggestions will be explored in the immediate future and any solution found will be announced as soon as possible.

The basic outlines of the proposed symposium as prepared by the officers of the Commission on Manganese follow; suggestions as to improvement or modifications or deletions would be greatly appreciated. Correspondence on this subject should be addressed to Prof. Grasselly or to the other officers as convenient.

DR. I. M. VARENSOV
Secretary

Geological Institute of the Academy
of Sci. of USSR
Pyzhevsky pereulok 7,
Moscow Zh-17, USSR

DR. JOHN VAN N. DORR II
Vice-President

US Geological Survey, Washington,
D. C. 20242, USA

PROF. DR. GY. GRASELLY
President

Inst. of Mineralogy, Geochemistry
and Petrography,
University of Szeged
Táncsics M. u. 2., Szeged, Hungary