THE CANADIAN MINERALOGIST

Journal of the Mineralogical Association of Canada

Volume 17 | November 1979 | Part 4

Canadian Mineralogist
Vol. 17, pp. 673-677 (1979)

SERPENTINE MINERALOGY, PETROLOGY AND PARAGENESIS

Proceedings of a symposium sponsored by the Mineralogical Association of Canada, held on October 25, 1978 during the joint annual meeting of the Geological Association of Canada, the Mineralogical Association of Canada and the Geological Society of America, October 23-26, in Toronto.

INTRODUCTION

The papers published in this volume cover a wide, but representative, selection of topics, from serpentine mineral structures and chemistry to the petrology, tectonic history and evolution of serpentinites. Of the 15 papers presented here one, by Labotka and Albee, was presented during the meeting but was not originally part of the symposium, and two delivered at the symposium were not submitted for publication. Abstracts of these papers, by Duke (1978) and Evans & Trommsdorff (1978), can be found in the Abstracts for the meeting.

In a sense all the papers are based on Whittaker & Zussman's (1956) paper on the serpentine minerals, where a classification based on the structures of the minerals was established for the first time. This classification divided the serpentine minerals into three structural types: chrysotile with a cylindrical structure, antigorite with an alternating-wave structure, and lizardite, a previously unrecognized mineral, with a flat structure. Chrysotile was found to occur most frequently as clinochrysotile, a 2-layer structure of identical layers with *a* parallel to the cylindrical or fibre axis (Whittaker 1956a), less frequently as orthochrysotile, a 2-layer structure with 180° rotations between layers with *a* parallel to the fibre axis (Whittaker 1956b), and least frequently as parachrysotile, a 2-layer structure with 180° rotations between layers and with *b* parallel to the fibre axis (Whittaker 1956c). Later, Wicks & Whittaker (1975) reexamined the earlier classification in the light of subsequent research and reaffirmed the threefold division on the basis of structure. Chrysotile, parachrysotile and lizardite were found to be polymorphs because their structures involve different mechanisms of misfit relief to overcome the difference in size between the larger octahedral sheet and the smaller tetrahedral sheet. Antigorite is not a polymorph of the other serpentines but is a phase of a slightly but essentially different composition, with the difference in composition being related to the wavelength of the alternating-wave structure. Detailed examination of the chrysotile and lizardite structures emphasized certain structural similarities between the minerals, in spite of the cylindrical nature of chrysotile, but pointed out that there is a slight, but fundamental, difference between the stacking in chrysotile and that in lizardite. Based on this difference in stacking, all flat structures, 1- and 2-layer lizardites and the multilayer serpentines can be regarded as polytypes of lizardite, and the cylindrical structures, 1- and 2-layer clinochrysotile and orthochrysotile, can be regarded as polytypes of chrysotile. Thus, in terms of polytype nomenclature, clinochrysotile would become chrysotile–$2M_{c1}$ or, rarely, chrysotile–$1M_{c1}$ and orthochrysotile, chrysotile–$2Or_{c1}$. One-layer lizardite would be lizardite–$1T$ with more complex structures designated, for example, as lizardite–$6T_1$ (Bailey 1969, Hall *et al.* 1976). Both the polytype nomenclature and the older chrysotile nomenclature are used in this volume.

The importance of the difference in stacking between chrysotile and lizardite has been emphasized by the research of Middleton & Whittaker (1976) and Cressey & Zussman (1976) on the nature of Povlen-type, polygonal chrysotiles. Both cylindrical cores of chrysotile–$2M_{c1}$ with polygonal outer zones of chrysotile–$2M_{c1}$ and cylindrical cores of chrysotile–$2Or_{c1}$ with polygonal outer zones of lizardite–$2H$ were observed. Thus chrysotile- and lizardite-type stacking were observed within the same fibre, and chrysotile-type stacking was found within the curved layers of the cylindrical core and within the flat layers of the polygonal zone.

One further point should be added. The term ortho-antigorite was introduced by Brindley & von Knorring (1954) to describe a serpentine with a large superlattice. It was very quickly shown by Zussman & Brindley (1957) that this material was not antigorite but rather a 6-layer orthohexagonal serpentine. It is a polytype of lizardite and has been described in detail as lizardite–$6T_1$ by Hall *et al.* (1976). In spite of the rather prompt discreditation of ortho-antigorite and subsequent work on this material, the term persists in the literature and its misuse has led to confusion on more than one occasion in recent years.

For those interested in further details on the serpentine minerals and serpentinites, reviews by Coleman (1971, 1977), Moody (1976) and Evans (1977) are useful. A discussion of serpentine diffraction-patterns is given by Wicks (1979) and a well-documented temperature – pressure phase diagram was presented by Evans *et al.* (1976). Important mineral–aqueous solution equilibria studies have been carried out by Hemley *et al.* (1977a, b) and Nesbitt & Bricker (1978).

A brief description of each of the 15 papers is given in the order in which they appear in the volume and brief references are made to closely related published work.

Yada's well-known high-resolution electron microscopy (Yada 1967, 1971) has been carried a step further in its development by his use of image-processing techniques to achieve atomic resolution of Si and Mg in clino- and orthochrysotile. The arrangements of alternate layers are clearly displayed and confirm the general features of the structure refinement carried out with X-ray diffraction by Whittaker (1953). The alternating-wave structure of antigorite was also resolved, confirming Kunze's (1961) structure refinement.

Middleton & Whittaker investigated individual fibres of parachrysotile by electron diffraction and obtained, for the first time, a complete diffraction pattern without additional reflections from normal chrysotile. The electron-diffraction patterns confirm the earlier X-ray work of Whittaker (1956c), which was based on a limited number of reflections. The results indicate that parachrysotile may have a range of structures, from purely cylindrical to predominantly polygonal, similar to those described for Povlen-type clinochrysotile and orthochrysotile (Middleton & Whittaker 1976, Cressey & Zussman 1976).

The relationship of the intergrowth of brucite and chrysotile in the fibrous variety of brucite *nemalite*, as investigated by electron microscropy and diffraction, is reported by Whittaker and Middleton. The results suggest that the brucite might have formed in association with parachrysotile (which has largely recrystallized to normal chrysotile). The formation of fibrous magnesite may have been controlled by chrysotile fibres between which the magnesite grew and which it partly replaced.

Peterson, Hill and Gibbs present molecular-orbital calculations for the brucite and gibbsite structures and for a flat serpentine structure, and thus continue, with a more rigorous analysis, some of the structural discussions of Radoslovich (1963a, b) and Wicks & Whittaker (1975).

Mössbauer analyses of chrysotile asbestos from several Canadian localities have been carried out by Blaauw, Stroink, Leiper and Zentilli who have found that Fe^{2+} occurs only in octahedral sites and that Fe^{3+} is distributed between octahedral and tetrahedral sites. Their Mössbauer results on the oxidation state of iron are significantly different from the published chemical analyses and suggest that the trends in the oxidation state of iron in serpentines noted by Whittaker & Wicks (1970), based on wet-chemical analyses, may not be as rigorous as originally suggested. This is further substantiated in a recent paper by Rozenson *et al.* (1979) who have found the same discrepancies between Mössbauer and wet-chemical analyses in some of the same samples examined by Whittaker & Wicks (1970).

Golightly and Arancibia trace the migration of elements during serpentinization and weathering of a lherzolite to a nickeliferous laterite. Unlike earlier studies based on collections of specimens from a variety of localities (Brindley & Pham Thi Hang 1973, Springer 1974) Golightly and Arancibia relate their samples to the weathering profile. Infrared studies of nepouite are interpreted based on the assignment of absorption bands in lizardite by Yariv & Heller-Kallai (1975).

In his first paper Dungan gives a description of lizardite bastites after orthopyroxene, clinopyroxene and amphiboles that augments the discussion of Wicks & Whittaker (1977). Many of the clinopyroxene and amphibole bastites have associated secondary diopsides of similar compositions to those found in association with antigorite (Peters 1968, Evans & Trommsdorff 1970). However, in this case, Dungan suggests that they have formed in the retrograde environment with lizardite, as the metastable analogue of the prograde antigorite + secondary diopside assemblage.

The application of transmission electron-microscopy to ion-thinned samples of rock-forming and some vein-forming serpentine has been carried out by Cressey on samples previously studied by Wicks & Whittaker (1977) with the microbeam X-ray camera. Lizardite, normal chrysotile, Povlen-type chrysotile, fine-grained serpentine and antigorite were found in different textures, but important details on the nature of the serpentinization of olivine were also discovered. Olivine is replaced in a two-stage process rather than the single-stage process described by Wicks *et al.* (1977). In the first stage fine-grained, poorly-formed serpentine is formed; as the serpentinization front advances, this recrystallizes in the second stage to coarsely crystalline, well-oriented lizardite.

In an earlier study Chernosky (1975) examined the system $MgO–Al_2O_3–SiO_2–H_2O$. In the study by Caruso and Chernosky in this volume a combination of laboratory synthesis of lizardite, thermodynamic calculations and field observations is used to suggest that Al-lizardite may be stable with respect to chlorite + low Al-antigorite in serpentinites recrystallized at low pressures.

Dungan's second paper, an extension of earlier studies (Dungan 1977), presents microprobe analyses of antigorites and lizardites ± minor chrysotile in mesh textures, orthopyroxene bastites and clinopyroxene bastites. The compositional differences between the pseudomorphic serpentines and the antigorites were found to reflect the difference between the lizardite and chrysotile structural formulae and that of antigorite. The Al and Cr contents of the serpentine in the bastites are higher than the serpentine in the mesh textures; this higher Al may increase its thermal stability with respect to antigorite, as has been suggested by Caruso & Chernosky in this volume.

A similar microprobe study of serpentine compositions on a wider variety of textural assemblages, all identified by microbeam X-ray camera, was undertaken by Wicks and Plant. As was the case in the studies of Golightly and Arancibia and Dungan, in this volume, relatively high amounts of Al and Cr were noted in the retrograde lizardite bastites. The criteria given by Wicks & Whittaker (1977) for the optical identification of lizardite bastites formed in retrograde environments were found to be valid. However, bastites affected by prograde regimes, although chemically and visually similar to retrograde bastites, may be mineralogically different; thus the criteria of Wicks & Whittaker (1977) can only be used for retrograde bastites. Different prograde bastites were found to be composed of lizardite, a chlorite-like mineral + antigorite, or Povlen-type chrysotile. The analyses of mineral compositions confirm some of the trends noted by Whittaker & Wicks (1970), revise others and extend the observed (mainly Fe) substitution. A stability field for lizardite similar to that of chrysotile is suggested.

Labotka and Albee have performed mass-balance calculations on bulk compositions of a partly serpentinized dunite that contains zones of antigorite + magnetite + brucite serpentinite and chrysotile-asbestos veins. The results indicate that magnesium was conserved and silica and water were added. They conclude that this serpentinization was neither isovolumetric nor isochemical.

A complex history of retrograde, then prograde, followed by retrograde serpentinization and carbonatization in ultramafic rocks from Bird River, Manitoba, is described by Coats and Buchan. This history is interpreted in terms of the $CaO–MgO–SiO_2–H_2O–CO_2$ system studied by Trommsdorff & Evans (1977).

Laurent and Hébert describe an early oceanic, partial serpentinization of the ophiolite ultramafic rocks of the Québec Appalachians, followed by late continental, complete serpentinization and asbestos-vein development during emplacement by obduction of the ophiolite suite onto the continental margin. The two stages of serpentinization are in general agreement with the early retrograde, followed by later prograde serpentinization and asbestos-vein development described in the Québec asbestos mines by Wicks and Plant.

Finally, Moody has extensively reviewed several aspects of ophiolite metamorphism, extending the earlier review of ophiolites by Coleman (1977). She concludes that metamorphism of the upper part of the ophiolite sequences could occur within the ocean, but that metamorphism and serpentinization of the ultramafic layer of the sequence probably occurred after obduction onto the continental margin.

ACKNOWLEDGEMENTS

The idea of organizing a symposium on serpentine minerals during the joint annual meeting of the GSA/GAC/MAC was first suggested to me by J. A. Mandarino. The sponsorship and financial support of the Mineralogical Association of Canada and the help and encouragement of the Executive through all stages of this project are very gratefully acknowledged. Several of the participants would not have been able to attend had not Asbestos Corporation Limited, Cassiar Asbestos Corporation Limited, Cominco Limited, the Ontario Research Foundation, Riocanex, the Royal Ontario Museum and Texasgulf Incorporated contributed funds. I am particularly appreciative of their interest and support.

Publication of the symposium was assured through a generous publication grant from the Geological Survey of Canada, and through the efforts of the editors of the Canadian Mineralogist.

F. J. Wicks, *editor.*

REFERENCES

BAILEY, S.W. (1969): Polytypism of trioctahedral 1:1 layer silicates. *Clays Clay Minerals* **17**, 355-371.

BRINDLEY, G.W. & PHAM THI HANG (1973): The nature of garnierites. I. Structures, chemical compositions and color characteristics. *Clays Clay Minerals* **21**, 27-40.

——— & VON KNORRING, O. (1954): A new variety of antigorite (ortho-antigorite) from Unst, Shetland Islands. *Amer. Mineral.* **39**, 794-804.

CHERNOSKY, J.V., JR. (1975): Aggregate refractive indices and unit cell parameters of synthetic serpentine in the system $MgO–Al_2O_3–SiO_2–H_2O$. *Amer. Mineral.* **60**, 200-208.

COLEMAN, R.G. (1971): Petrologic and geophysical nature of serpentinites. *Geol. Soc. Amer. Bull.* **82**, 897-918.

——— (1977): *Ophiolites: Ancient Oceanic Lithosphere?* Springer-Verlag, New York.

CRESSEY, B.A. & ZUSSMAN, J. (1976): Electron microscopic studies of serpentinites. *Can. Mineral.* **14**, 307-313.

DUKE, J.M. (1978): Serpentinization of the Dumont ultramafic intrusion, N. W. Quebec. *Geol. Assoc. Can./Mineral. Assoc. Can. Program Abstr.* **3**, 392.

DUNGAN, M.A. (1977): Metastability in serpentine–olivine equilibria. *Amer. Mineral.* **62**, 1018-1029.

EVANS, B.W. (1977): Metamorphism of alpine peridotite and serpentinite. *Ann. Rev. Earth Planet. Sci.* **5**, 397-447.

———, JOHANNES, W., OTERDOOM, H. & TROMMSDORFF, V. (1976): Stability of chrysotile and antigorite in the serpentinite multisystem. *Schweiz. Mineral. Petrog. Mitt.* **56**, 79-93.

——— & TROMMSDORFF, V. (1970): Regional metamorphism of ultramafic rocks in the central Alps: parageneses in the system $CaO–MgO–SiO_2–H_2O$. *Schweiz. Mineral. Petrog. Mitt.* **50**, 481-492.

——— & ——— (1978): Petrology of antigorite serpentinites. *Geol. Assoc. Can./Mineral. Assoc. Can. Program Abstr.* **3**, 398.

HALL, S.H., GUGGENHEIM, S., MOORE, P. & BAILEY, S.W. (1976): The structure of Unst-type 6–layer serpentines. *Can. Mineral.* **14**, 314-321.

HEMLEY, J.J., MONTOYA, J.W., CHRIST, C.L. & HOSTETLER, P.B. (1977a): Mineral equilibria in $MgO–SiO_2–H_2O$ system. I. Talc–chrysotile–forsterite–brucite stability relations. *Amer. J. Sci.* **277**, 322-351.

———, ———, SHAW, D.R. & LUCE, R.W. (1977b): Mineral equilibria in the $MgO–SiO_2–H_2O$ system. II. Talc–antigorite–forsterite–anthophyllite–enstatite stability relations and some geologic implications in the system. *Amer. J. Sci.* **277**, 353-383.

KUNZE, G. (1961): Antigorit. Strukturtheoretische Grundlagen und ihre praktische Bedeutung für die weitere Serpentin-Forschung. *Fortschr. Mineral.* **39**, 206-324.

MIDDLETON, A.P. & WHITTAKER, E.J.W. (1976): The structure of Povlen-type chrysotile. *Can. Mineral.* **14**, 301-306.

MOODY, J.B. (1976): Serpentinization: a review. *Lithos* **9**, 125-138.

NESBITT, H.W. & BRICHER, O.P. (1978): Low temperature alteration processes affecting ultramafic bodies. *Geochim. Cosmochim. Acta* **42**, 403-409.

PETERS, T. (1968): Distribution of Mg, Fe, Al, Ca and Na in coexisting olivine, orthopyroxene and clinopyroxene in the Totalp serpentinite (Davos, Switzerland) and in the alpine metamorphosed Malenco serpentinite (N. Italy). *Contr. Mineral. Petrology* **18**, 65-75.

RADOSLOVICH, E.W. (1963a): The cell dimensions and symmetry of layer-lattice silicates. IV. Interatomic forces. *Amer. Mineral.* **48**, 76-99.

——— (1963b): The cell dimension and symmetry of layer-lattice silicates. VI. Serpentine and kaolinite morphology. *Amer. Mineral.* **48**, 368-378.

ROZENSON, I., BAUMINGER, E.R. & HELLER-KALLAI, L. (1979): Mössbauer spectra of iron in 1:1 phyllosilicates. *Amer. Mineral.* **64**, 893-901.

SPRINGER, G. (1974): Compositional and structural variations in garnierites. *Can. Mineral.* **12**, 381-388.

TROMMSDORFF, V. & EVANS, B.W. (1977): Antigorite-ophicarbonates: phase relations in a portion of the system $CaO–MgO–SiO_2–H_2O–CO_2$. *Contr. Mineral. Petrology* **60**, 39-56.

WHITTAKER, E.J.W. (1953): The structure of chrysotile. *Acta Cryst.* **6**, 747-748.

——— (1956a): The structure of chrysotile. II. Clinochrysotile. *Acta Cryst.* **9**, 855-862.

——— (1956b): The structure of chrysotile. III. Orthochrysotile. *Acta Cryst.* **9**, 862-864.

——— (1956c): The structure of chrysotile. IV. Parachrysotile. *Acta Cryst.* **9**, 865-867.

——— & Wicks, F.J. (1970): Chemical differences among the serpentine "polymorphs": a discussion. *Amer. Mineral.* **55**, 1025-1047.

——— & Zussman, J. (1956): The characterization of serpentine minerals by X-ray diffraction. *Mineral. Mag.* **31**, 107-126.

Wicks, F.J. (1979): Mineralogy, chemistry and crystallography of chrysotile asbestos. *In* Short Course in Mineralogical Techniques of Asbestos Determination (R. L. Ledoux, ed.), *Mineral. Assoc. Can. Short Course* **4**, 35-78.

——— & Whittaker, E.J.W. (1975): A reappraisal of the structures of the serpentine minerals. *Can. Mineral.* **13**, 227-243.

——— & ——— (1977): Serpentine textures and serpentinization. *Can. Mineral.* **15**, 459-488.

———, ——— & Zussman, J. (1977): An idealized model for serpentine textures after olivine. *Can. Mineral.* **15**, 446-458.

Yada, K. (1967): Study of chrysotile asbestos by a high resolution electron microscope. *Acta Cryst.* **23**, 704-707.

——— (1971): Study of microstructure of chrysotile asbestos by high resolution electron microscopy. *Acta Cryst.* **A27**, 659-664.

Yariv, S. & Heller-Kallai, L. (1975): The relationship between the i.r. spectra of serpentines and their structures. *Clays Clay Minerals* **23**, 145-152.

Zussman, J. & Brindley, G.W. (1957): Serpentines with 6-layer ortho-hexagonal cells. *Amer. Mineral.* **42**, 666-670.

Received November 1979.