

COMMENTS ON SERPENTINIZATION AND RELATED METASOMATISM

P. Černý, *Geological Institute, Czechoslovak Academy of Sciences, Praha, Czechoslovakia.*

ABSTRACT

In highly metamorphosed regions, alpine peridotites are serpentized after consolidation of the enclosing siliceous rocks, under much lower p - T conditions than existed during the preceding regional metamorphism. Magnesium outflow during an essentially equal volume serpentization often causes chloritization and zeolitization of surrounding rocks. On the other hand, in low-grade metamorphic and sedimentary environment serpentization takes place during the tectonic emplacement of ultramafic bodies and yields rodingite and jadeite zones that were produced by calcium outflow from completely serpentized ultramafites.

Some contact reactions of "cold-intrusive" ultramafites with adjacent siliceous rocks take place above the serpentization p - T range and some within its limits. Above the p - T range, the products and extent of the reaction are controlled by the overall "activity" of the surrounding siliceous rocks—*e.g.*, granulites, migmatites, plutonic masses; the reaction is essentially that of contact equilibration. Within the p - T limits of serpentization this process combines with metasomatism caused by components released upon concomitant serpentization. Resulting contact assemblages are extremely variable with regard to varying metamorphic grade, tectonic mobility, and other factors.

Specific serpentine minerals seem to be formed by certain serpentization processes, depending on static versus shear pressures and on generally lower versus higher p - T conditions. Recent investigation shows, however, that these relations are much more complicated than previously supposed. Breakdown of chrome spinel to Cr-chlorite + magnetite proceeds dominantly in pre-serpentization stages. If contemporaneous with serpentization, Cr-chlorite is regarded as a metastable transient phase.

INTRODUCTION

The recent discussion on serpentization (Hostetler *et al.*, 1966; Coleman, 1966; Thayer, 1966 and 1967; Page, 1967 a, b) points out certain phenomena that merit careful consideration. This paper contributes several related facts and ideas, namely: serpentization of and Mg-metasomatism around deep-seated ultramafites as compared with Ca-removal and rodingitization in the course of serpentization at higher levels of the crust; general characteristics of mutual contact reactions; selective formation of serpentine minerals under various conditions, and their relation to the breakdown of chrome spinels. Reports on some of the particular ultramafites and on the associated metasomatic phenomena studied will be given elsewhere in more detail.

SERPENTINIZATION OF DEEP-SEATED ULTRAMAFITES

This discussion is based on experience gained from ultramafites located along the eastern margin of Moldanubicum and in the adjacent Svratka

anticline, in Western Moravia, Czechoslovakia. The ultramafites compose isolated bodies mostly of much less than 1 a square kilometer in area, seated in katametamorphosed gneisses, migmatites, and granulites. General geology of the enclosing metamorphic series is given by Svoboda *et al.* (1966), regional tectonic setting of the ultramafites is discussed by Weiss (1966).

The earliest perioditic assemblages, well preserved in most investigated ultramafites, range from dunite to various peridotite compositions. The pyrope+diopside+enstatite, enstatite+spinel, enstatite+spinel+amphibole, and enstatite+amphibole+(Cr-chlorite+magnetite) assemblages are most frequent, the last two often showing gradational transitions. Their metamorphic fabric is usually not related to local and regional structures; only locally the orientation of the Cr-chlorite+magnetite association coincides with the schistosity of surrounding gneissic rocks.

Serpentinization produced lizardite and chrysotile that preserve the original "anhydrous" framework of the ultramafites. Antigorite was not encountered, brucite was detected only in the least serpentinized rocks. Slickensided veinlets of six-layer orthoserpentine often cut the mesh-textured serpentinites; they are very late but still preceded the formation of the rare cross-fiber chrysotile veinlets.

Along their contacts with the country-rocks, ultramafites are rimmed by successive bands of anthophyllite, tremolite-actinolite, and phlogopite. The cross-fiber fabric of the amphiboles in these contact zones, similar to that described by Rost (1966), often becomes schistose when adjacent to the country rock. The contact assemblage is sometimes concentrated in the pressure shadows of the ultramafic bodies.

The feldspar and quartz of the gneissic rocks closely adjacent to the serpentinites are replaced by extremely fine-grained chlorite and saponite. The fabric of the gneisses is well preserved upon the conversion. When extensive, these chlorite+saponite zones are accompanied by a zone of sodic zeolites, prehnite, and beta-cerolite. This assemblage replaces the felsic constituents of gneisses and fills fine fissures in a broader neighbourhood of the chloritized band.

The same alteration was described from veinlets of desilicated pegmatites that penetrate perioditites (Matthes, 1940; Černý and Povondra, 1965 a, b). In Western Moravia, the feldspar veins are replaced by penninite, saponite, prehnite, and beta-cerolite with clinocllore, harmotome, and hydrotalcite in tiny cracks. Such alteration to magnesian layer-silicates was observed also on other diorite-like veins and on tectonic inclusions of gneisses.

More extensive chloritization and particularly the subsequent zeolitization took place, however, only in a suitable spatial setting. Pegmatitic veinlets and deep protrusions of country rocks are usually highly altered but along simple straight-lined contacts the chlorite+saponite assemblage may become barely detectable.

All evidence available from field and laboratory data and from recent studies on the serpentinization p - T range indicates that the examined ultramafites underwent a complicated metamorphic evolution before attaining the present setting, fabric, and mineral composition. Their tectonic emplacement and concomitant development of banded reaction rims took place under at least amphibolite facies conditions. Later serpentinization proceeded during a regional uplift and simultaneous decrease of p - T conditions, without chance of any notable expansion in a consolidated, rigid gneissic environment. Under such conditions serpentinization is believed to be a long-lasting process, unaided by dynamo-metamorphism and promoted only by pore fluids, and is far from completed.

Magnesium released by serpentinization apparently causes chloritization and saponitization of adjacent siliceous rocks. Calcium and alkali metals expelled from siliceous rocks during this magnesium metasomatism sometimes stimulate zeolitization in broader neighbourhood of the chloritized zones. Extensive development of these metasomatic processes seems to be restricted to places suitable for higher concentration of the released magnesium.

In general, these observations and derived conclusions support Thayer's (1966, 1967) idea that magnesium can be removed from ultramafites in large quantities during serpentinization but need not react extensively with the surrounding siliceous rocks.

Mg-METASOMATISM AND RODINGITIZATION

The above relations contrast remarkably to the conditions favourable for the formation of rodingites, as summarized by Coleman (1963, 1966). These Ca, Mg-rich rocks originate in highly sheared ultramafites, in the course of their tectonic ascent and during their serpentinization. This may involve volume expansion and may be nearly completed. In my opinion, rodingites are formed not only by the action of constituents released upon serpentinization on the country rock but also by contemporaneous equilibration at the ultramafite-country rock contact.

Zeolitization evoked by the magnesium metasomatism in Moravian occurrences can be correlated with jadeite formation ahead of rodingites, caused by a similar sodium outflow from the rodingitized rocks (Coleman,

1961 and 1963; Thayer, 1966). The importance of shearing for jadeite formation was suggested and other conditions not favourable for zeolitization were quoted by Coleman (1961).

The most striking dissimilarity of the above processes is the Mg *versus* Ca metasomatism of country rock, both ascribed to alkali earths released from ultramafites during serpentinization. The different grade of serpentinization and discontinuous release of Ca may be the answer.

The Moravian ultramafites are less serpentinized than the described rodingite-producing bodies. In accordance with Thayer's (1966, 1967) statement that Ca-silicates are usually the last phases serpentinized, pyroxenes and particularly Ca-rich amphiboles resist alteration in the Moravian rocks. Thus the alteration of country rock by Ca-poor solutions involves no immediate calcium metasomatism in these localities; prehnite associated with zeolites in the front zone originated by expulsion of calcium from the chloritized gneisses.

On the contrary, Coleman (1961, 1966), Sokolova (1960), Dal Piaz (1967), and others describe the rodingite-bearing ultramafites as being quantitatively serpentinized, at least in their wide sheared margins. The homogenizing process in the sense of Thayer (1966, 1967) was finished in these rocks and calcium was forced to migrate almost quantitatively into the surrounding rocks. A selective outflow of Ca seems, however, unbelievable under such conditions. Extensive shearing in margins of ascending bodies has to initiate considerable migration of most reacting constituents; a voluminous removal of magnesium might take place in these cases, too.

As to the expansion *versus* constant volume serpentinization, Thayer (1967) is undoubtedly right in stating that preservation of original peridotite structure is prerequisite for evaluation of volume relations. For this reason it is rather doubtful if expansion could be calculated just in those ultramafites whose geological history and considerable brucite content favour this possibility (*e.g.*, the Great Ultramafic Belt of New Zealand). Coleman (1966, p. 81) recognized these difficulties when computing antigorite after olivine in the Anita Bay mylonitic dunite. On the other hand, ultramafites with well preserved pre-serpentinization structures are just those which seem to preclude any chance of substantial expansion.

This brief comparison of serpentinization proceeding under considerably diverse conditions clearly indicates the difficulties encountered in summarizing the general characteristics of this process. "Side effects" of serpentinization proper—*e.g.*, volume changes of ultramafites, gain and loss of constituents, metasomatism of country rocks, dissemination of released compounds without traceable mineralization of adjacent rocks—

seem to be remarkably different in diverse geological setting and must be treated with much caution.

GENERAL TRENDS IN CONTACT REACTIONS

The well-recognized "cold-intrusive" nature of many alpine ultramafites and their tectonic emplacement suggest that essentially two types of reactions at the contacts of such bodies with enclosing siliceous rocks may be distinguished: those proceeding above the p - T range of serpentinization and the others that take place within its limits.

In the first case, the reaction is essentially that of a contact equilibration, the extent and products of which are controlled mainly by the "activity" of the acid country rocks (Rost, 1966). Border zones formed by such reactions are frequent in regions metamorphosed in the amphibolite and higher facies. The contact reaction is considerably pronounced in migmatites and plutonic rocks; in such cases its products are almost the same as those found in pegmatite-ultramafite contacts. The anthophyllite+tremolite-actinolite+phlogopite rims around West-Moravian ultramafites, the same assemblage in Austria and Southern Bohemia (Fediuková, 1965; Rost, 1966), and probably the biotite+actinolite border zones described from Vermont (Phillips and Hess, 1936) belong to this group, to name at least some examples. As already shown, the subsequent metasomatism of country rock related to serpentinization is easily discernible from these processes.

This is not true, however, when the contact equilibration proceeds more or less contemporaneously with serpentinization. It is the writer's belief that in such occurrences where this simultaneity can be proved (*e.g.*, most New Zealand ultramafites described by Coleman, 1966) the resulting banded assemblages are produced not only by outflow of components released during serpentinization but also by equilibration of the adjacent ultramafite-country rock surfaces.

The chlorite+talc±tremolite±carbonate assemblage that occurs characteristically in low-grade schists (Phillips and Hess, 1936, and many others) is usually—but does not have to be—superimposed on already serpentinized ultramafites. When schistose, this assemblage is associated mostly with antigoritic serpentinites. It originates also at the expense of earlier anthophyllite+phlogopite zones. Besides temperature, the talc versus anthophyllite relationship is undoubtedly influenced also by shearing and availability of water and CO₂ (Yoder, 1952; Fyfe, 1962; Greenwood, 1963). Further intricacies of steatitization are illustrated by, *e.g.*, Bennington (1956), and Naldrett (1966). Generally, this group of contact reaction products is intermediate between the two described above.

SELECTIVE FORMATION OF SERPENTINE MINERALS

As generally accepted, antigorite originates and is stable in the high green-schist and albite-epidote-amphibolite facies environment. Stress or shearing seem not to be a prerequisite (*e.g.*, Green, 1961), nevertheless in most instances they partake in antigorite's formation. It originates on account of other serpentine minerals that seem to prefer an essentially static environment (*e.g.*, Green, 1961—lizardite and chrysotile; Hahn-Weinheimer and Rost, 1961; Mísař, 1966) or after primary olivine and pyroxenes (Coleman, 1966, and others). In lower grade metamorphism, massive ultramafites consist predominantly of lizardite, whereas shearing produces preferentially chrysotile, as evident from Coleman's (1966) observations.

This experience suggests that serpentine minerals are selected by both general metamorphic grade and character of pressures: higher static metamorphism—lizardite \pm chrysotile; higher dynamometamorphism—antigorite; lower static metamorphism—lizardite; lower dynamometamorphism—chrysotile. The position of the six-layer orthoserpentine, which seems to be much more widespread than previously supposed, is still not clear. These preferences might be of general validity. The role of chemical environment cannot be neglected but its actual significance in serpentinization of aluminum-poor anhydrous ultramafites is still unknown. The above ideas are consistent with Page's (1967 a) statement that antigoritic serpentinites generally occur in rocks above the high green-schist facies whereas lizardite+chrysotile serpentinite occur in lower grade environment. It must be added, however, that lizardite +chrysotile serpentinites also occur in amphibolite and granulite facies regions but are not formed under these conditions, but in lower-grade static retrogressive metamorphism.

Recent progress in serpentine mineralogy (*e.g.*, Jahanbagloo and Zoltai, 1968; Aumento, 1967) and reports on rock-forming occurrences of supposedly rare serpentine minerals (Krstanović and Pavlovic, 1967) indicate that the overall picture of mineral selection in serpentinized rocks may become considerably complicated in the near future.

BREAKDOWN OF CHROME SPINEL AND SERPENTINIZATION

Thayer (1966) assumes that chromite behaves differently in antigoritic and mesh-textured lizardite+chrysotile serpentinites. These differences are probably related rather to the earlier, pre-serpentinization events as shown by Rost (1961, 1963). This author claims that the breakdown of chrome spinel to Cr-chlorite+magnetite requires higher temperatures than those required for serpentinization, and proved it in numerous European occurrences. Grade of the chromite alteration and resulting

assemblages are governed primarily by availability of water in the closely preceding pre-serpentinization stage, by the character of concomitant pressures, and only then by the complexity of further evolution of the ultramafic rock. In addition the ultramafites of the Svatka anticline can be contrasted to Thayer's examples. They consist of mesh-textured serpentinite with chrome spinel either unaffected, or converted to radiating clusters of Cr-chlorite with magnetite cores, or altered to thin Cr-chlorite+magnetite streaks where there was a pronounced late but pre-serpentinization shearing.

Since antigorite originates in a higher metamorphic environment than mesh-textured serpentine minerals, there might be some chance that the breakdown of chrome spinel to Cr-chlorite+magnetite could be at least partially contemporaneous with antigoritization. Such relations are to be looked for in localities with anhydrous peridotitic assemblages transformed directly to antigorite serpentinite. Even in such cases, however, Cr-chlorite must be regarded as a metastable transitional phase. Rost (1961) has clearly shown that Cr-chlorite preserved in mesh-texture serpentinites vanishes readily upon antigoritization of the parent rock, being also replaced by antigorite. Instability of a high-aluminum chlorite in a prevailing low-aluminum serpentine environment is evident also from studies of Roy and Roy (1955), Gillery (1959), and others who have examined the breakdown of chlorite to Al-serpentine in low p - T ranges.

CONCLUDING REMARKS

Deciphering all the factors that govern the course of serpentinization and influence the formation of ultramafite-country rock contacts is often nearly unrealizable. Coleman (1966, p. 74-75) is well aware of the problems met in the study of rodingites in alpine-folded regions: influence of structure, fluids, and rock composition, of tectonic instability of ultramafites and changing p - T conditions during their ascent, leaving behind of early and formation of new metasomatic contacts. Adding also the complexities encountered in metamorphic regions—much wider p - T range, changing nature of fluids, static versus dynamic metamorphism, progressive or retrograde sequence of superimposed metamorphic events and other factors—we see clearly that attempts to classify serpentinization and contact equilibration processes in more detail would be premature. Thorough investigation of serpentinized ultramafites and their contact assemblages in various geological environment is badly needed to furnish detailed data sufficient for quantitative physico-chemical treatment.

ACKNOWLEDGEMENTS

The early discussions with Professor F. Rost, Saarbrücken, and the obliging assistance and criticism given by Drs. R. G. Coleman and T. P. Thayer, U. S. Geological Survey, and by Professor S. Matthes, Würzburg are greatly acknowledged.

REFERENCES

- AUMENTO, F. (1967) A serpentine mineral showing diverse strain relief mechanism. *Amer. Mineral.*, **52**, 1399–1413.
- BENNINGTON, K. O. (1956) Role of shearing stress and pressure in differentiation as illustrated by some mineral reactions in the system $MgO-SiO_2-H_2O$. *J. Geol.*, **64**, 558–577.
- COLEMAN, R. G. (1961) Jadeite deposits of the Clear Creek area, New Idria District, San Benito County, California. *J. Petrology*, **2**, 209–247.
- (1963) Serpentinities, rodingites, and tectonic inclusions in Alpine-type mountain chains. *Geol. Soc. Amer. Spec. Pap.*, **73**, 130.
- (1966) New Zealand serpentinities and associated metasomatic rocks. *N. Zeal. Geol. Surv. Bull. n.s.* **76**, 102 p.
- ČERNÝ, P., AND P. POVONDRA (1965a) Harmotome from desilicated pegmatites at Hrubšice, Western Moravia. *Acta Univ. Carolinae-Geol.*, **1965**, 31–43.
- AND ——— (1965b) Chlorite and saponite replacing feldspars in West-Moravian desilicated pegmatites. *Acta Univ. Carolinae-Geol.*, **1965**, *Suppl.* **2**, 31–40.
- DAL PIAZ, D. G. (1967) Le “granatiti” (rodingiti l.s.) nelle serpentine delle Alpi occidentali italiane. *Mem. Soc. Geol. Ital.*, **6**, 267–313.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1962) *Rock-forming minerals*, Vol. 3, *Sheet Silicates*. Longmans, London.
- FEDIUKOVÁ, E. (1965) Ultrabasic xenoliths in the granulite at Mt. Kleř near Český Krumlov. *Acta Univ. Carolinae-Geol.*, **1965**, 189–202.
- FYFE, W. S. (1962) On the relative stability of talc, anthophyllite, and enstatite. *Amer. J. Sci.*, **260**, 460–466.
- GILLERY, F. H. (1959) The X-ray study of synthetic Mg-Al serpentines and chlorites. *Amer. Mineral.*, **44**, 143–152.
- GREEN, D. H. (1961) Ultramafic breccias from the Mesa Valley, Eastern Papua. *Geol. Mag.*, **98**, 1–26.
- GREENWOOD, H. J. (1963) The synthesis and stability of anthophyllite. *J. Petrology*, **4**, 317–351.
- HAHN-WEINHEIMER, P., AND F. ROST (1961) Akzessorische Mineralien und Elemente in Serpentin von Leupoldgrün (Münchberger Gneismasse). *Geochim. Cosmochim. Acta*, **21**, 165–181.
- HOSTETLER, R. B., R. G. COLEMAN, F. A. MUMPTON AND B. W. EVANS (1966) Brucite in Alpine serpentinities. *Amer. Mineral.*, **51**, 75–98.
- JAHANBAGLOO, I. C. AND T. ZOLTAI (1968) The crystal structure of a hexagonal Al-serpentine. *Amer. Mineral.*, **53**, 14–24.
- KRSTANOVIĆ, I. AND S. PAVLOVIĆ (1967) X-ray study of six-layer orthoserpentine. *Amer. Mineral.*, **52**, 871–876.
- MATTHES, S. (1940) Biotitführende Metabasiteinschaltungen in Serpentinivorkommen des sächsisch-fichtelgebirgischen Kristallins und ihre Ableitung. *Tschermak's Mineral. Petrogr. Mitt.*, **52**, 77–154.
- MĚSAŘ, Z. (1966) Structural history of ultrabasic bodies of the Letovice crystalline unit (Moravia). *Krystalinikum*, **4**, 109–125.
- NALDRETT, A. J. (1966) Talc-carbonate alteration of some serpentinized ultramafic rocks south of Timmins, Ontario. *J. Petrology*, **7**, 489–499.
- PAGE, N. J. (1967a) Serpentinization considered as a constant volume metasomatic process: a discussion. *Amer. Mineral.*, **52**, 545–549.
- (1967b) Serpentinization at Burro Mountain, California. *Contr. Mineral. Petrology* **14**, 321–342.

- PHILLIPS, A. H., AND H. H. HESS (1936) Metamorphic differentiation at contacts between serpentinite and siliceous country rocks. *Amer. Mineral.*, **21**, 333-362.
- ROST, F (1961) Chlorit und Granat in ultrabasischen Gesteinen. *Fortschr Mineral.*, **39**, 112-126.
- (1963) Ultrabasite der Kruste und ihr Mineralbestand. *N. Jahrb. Mineral., Monatsh.* **1963**, 263-272.
- (1966) Über ultrabasische Einschlüsse in metamorphen Gesteinen des südlichen Moldanubikums. *Krystalinikum*, **4**, 127-162.
- ROY, D. M., AND R. ROY (1955) Synthesis and stability of minerals in the system MgO—Al₂O₃—SiO₂—H₂O. *Amer. Mineral.*, **40**, 147-178.
- SOKOLOVA, L. A. (1960) Petrography of the Bazhenovo chrysotile-asbestos deposit and some problems of its metamorphism. *Trudy Inst. Rud. Mest., Petrogr., Mineral. Geokh.* **47**, 3-42. [in Russian].
- SVOBODA, J., *et al.* (1966) *Regional geology of Czechoslovakia, Vol. I, Czech Massif*. Academia, Praha.
- THAYER, T. P. (1966) Serpentinization considered as a constant volume metasomatic process. *Amer. Mineral.*, **51**, 685-710.
- (1967) Serpentinization considered as a constant volume metasomatic process: a reply. *Amer. Mineral.*, **52**, 549-553.
- WEISS, J. (1966) Ultrabasic rocks of the West-Moravian crystalline complex. *Krystalinikum*, **4**, 171-183.
- YODER, H. S., JR. (1952) The MgO—Al₂O₃—SiO₂—H₂O system and the related metamorphic facies. *Amer. J. Sci., Bowen Vol.*, 569-627.

Manuscript received, September 11, 1967; accepted for publication, April 12, 1968.