

Relation of minor-element content of serpentines to their geological origin*

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WE have been studying the serpentine group of minerals since 1943, as time permitted, in connection with several mineralogical and petrological problems. A large number of single specimens from worldwide localities and suites from various occurrences in the United States have been examined. Most of our data have been obtained from a collection of twenty chemically analysed serpentines (Table 1), but only part of the data is given here. We have made many differential thermal analyses, dehydration studies, X-ray powder diffraction patterns, and spectrographic analyses. Some of the results and conclusions of this study are incorporated in a paper by NAGY and FAUST (submitted to the editor of the *American Mineralogist*). The complete set of these data together with their correlation and interpretation will be published later by the U.S. Geological Survey.

The availability of this fine collection of analysed and selected materials offered an unusual opportunity to correlate the mineralogical and petrological data with the geochemistry of the specimens studied. This note presents the conclusions we have drawn from our research on the relation of minor elements to the kinds of rocks in which the serpentines are found.

The samples used in this study were all prepared by carefully crushing large fragments down to the size where the serpentine became unlocked from associated minerals. These grains were then handpicked under a binocular microscope or jeweller's loupe, and the purified samples crushed to a still finer size and re-examined. After the entire sample was crushed to pass through a 100-mesh-sieve, it was re-examined for impurities under the petrographic microscope. Almost all of the samples thus prepared contained no detectable impurities, but in a few samples small specks of chromite so finely divided as to preclude further purification were present. In only one specimen did the Cr_2O_3 amount to as much as 0.22%. If we assume that all of this Cr_2O_3 is present in chromite, and there are valid reasons to doubt this, then the maximum chromite content would have amounted to only 0.32%.

The name *serpentine* has various connotations. In this paper we use the word serpentine to refer to a member of the serpentine group of minerals. Ultrabasic rocks which contain a mineral (or minerals) of the serpentine group are here designated Class A, which includes dunites, pyroxenites, peridotites, and related rocks; the serpentine-bearing rocks of various types of metamorphic origins are designated Class B, which includes metamorphosed limestones and

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dolomites, contact metamorphic deposits, and hydrothermal veins. Our minor-element studies apparently do not differentiate between the serpentines of the two types of ultrabasic rocks within Class A, the alpine-type peridotites and the

Table 1. Localities of the specimens of serpentine group minerals studied

Sample No.	Class A (in ultrabasic rocks)	Sample No.	Class B (in metamorphosed limestones, dolomites, etc.)
F-1	State Line Pits, Lowes mine, approximately 1-2 miles west-northwest of Rock Springs, Cecil County, Maryland	F-8	Smithfield, Windsor County, Rhode Island
F-3	Near Forest Hill, Harford County, Maryland	F-13	Tilly Foster iron mine, near Brewster Station, Putnam County, New York
F-15	North of Domo d' Ossola in Val Antigorio, Novara Province, Piedmont Region, Italy	F-14	Pei-wa-ku and Lao-yeh-ling, Hsiu-yen Hsien, Liaoning Province, Manchuria
F-19	Bare Hills, Baltimore County, Maryland.	F-20	Asbestos deposits, Gila County, Arizona
F-40	Prairie Creek area of peridotite in T. 8° S., R. 25° W., 2½ miles south-southeast of Murfreesboro, Pike County, Arkansas	F-22	Turkey Hill, near Montville, Morris County, New Jersey
F-42	Near Norris, Tennessee	F-23	Dognácska, 10 km west from Reschitza, Hungary
F-43	Crump's Quarry, Mineral Hill, ¼ mile north of state road, about one mile west of Media, Middletown, Pennsylvania	F-24	Montville, Morris County, New Jersey
F-46	Near Bellows Falls, Windham County, Vermont	F-25	Montville, Morris County, New Jersey
F-47	Tyrol, Austria	F-41	Windous deposit, Currant Creek magnesite deposits, White Pine County, Nevada
		F-53	Asbestos deposits, Grand Canyon, Arizona (presumably from the same general area as F-20)
		F-56	Fifth level, at the shaft, Gouverneur Tale Company, Balmat, New York

alnoite, kimberlite, mica-peridotite suite (see HESS, 1955). Specimens F-40 and F-42, Table 1, belong to the later suite.

The process of serpentinization is usually defined as the formation of serpentine from pre-existing ferromagnesian or magnesian minerals by hydrothermal solutions.

Chlorite, talc, stevensite, saponite, and other hydrous magnesian silicates commonly occur with serpentine.

The specimens selected for the spectrographic study of the minor elements were those for which we have chemical analyses. Other spectrographic data on serpentines in our files were also considered in drawing our conclusions. We have divided the serpentine minerals into the two classes, previously mentioned, based on their origin. Class *A* contains nine specimens from localities where ultrabasic rocks crop out. These serpentines were formed by deuteric or subsequent hydrothermal alteration of the original ultrabasic rocks. Class *B* contains eleven

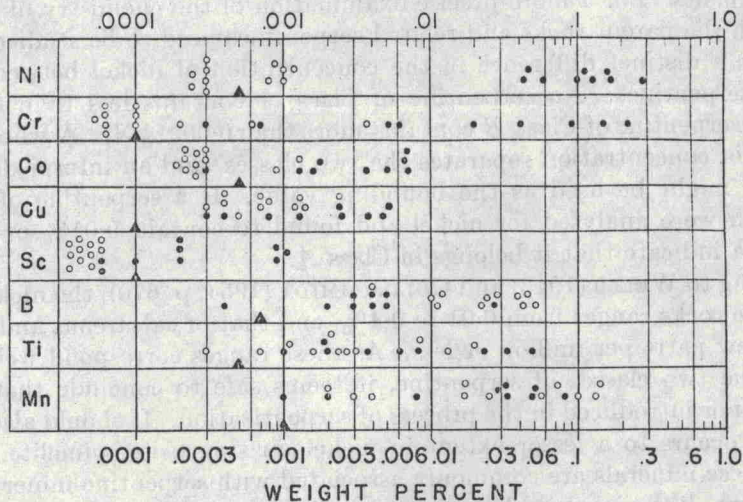


Fig. 1. Graphical representation of the concentration of some minor elements in the serpentine group minerals. Triangular black index represents sensitivity limit for the element. Points to the left of the index are samples in which the element was not detected. Solid circles represent serpentines associated with ultrabasic rocks. Empty circles represent serpentines from other rock associations.

specimens found chiefly in metamorphosed limestones and dolomites, in contact metamorphic deposits, and in hydrothermal veins. Except for the vein deposits, the serpentines have been formed by hydrothermal replacement of pre-existing ferromagnesian or magnesian minerals.

Spectrographic analyses were made for the following chemical elements: Ni, Cr, Co, Sc, Cu, B, Mn, Ti, Zr, Al, Ca, Ba, Zn, Ge, Ga, As, V, Na, and Be. In addition, mercury was determined for four serpentines of Class *A* and four of Class *B*. The following elements were not found: Ag, Au, Cd, In, Tl, Sn, Pb, Bi, Te, Pt, Mo, W, Nb, Y, Sb, La, Li, and P.

The data for eight elements in our study are given in Fig. 1.

The minor elements of serpentines are of unusual interest, because they were in part inherited from the parent rock that was serpentinized and in part introduced from external sources. Their study, therefore, provides valuable information regarding the chemistry of the serpentinization process.

In general, ultrabasic rocks, which are the parent rocks for Class *A* serpentines, are considerably richer in minor elements than magnesian limestones, which are the

parent rocks for many of the Class *B* serpentines. This difference in the composition of the parent rocks is retained more or less intact in the serpentines and explains the generally higher percentages of nickel, chromium, cobalt, and scandium in serpentines of Class *A*. The minor-element composition of the parent rocks of the samples studied is not known; hence, it is necessary to base the present discussion on (1) published, average compositions of such rocks and (2) mineralogical data and paragenetic studies. Some of the data in the literature on minor elements in ultrabasic rocks are based on samples that were serpentinized, but it has not been practical to eliminate such data and recompute the average abundances of the various elements. For a more precise examination of the chemistry of serpentinization, both the parent rocks and related serpentines need to be studied together.

There is a distinct difference in the concentration of nickel between the two classes of serpentines. No serpentine of Class *A* contains less than 0.04% Ni, whereas no serpentine of Class *B* contains more than 0.002% Ni. A whole order of magnitude of concentration separates the two classes, and an intermediate value, say 0.01%, might be used as the bounding value. If a serpentine of unknown classification were analysed for nickel and found to contain 0.01% or more, the present data indicate that it belongs in Class *A*.

According to WELLS (1943) and GOLDSCHMIDT (1954, p. 670), the nickel content of ultrabasic rocks ranges from 0.01 to 0.4%, and that of calcareous and dolomitic rocks is a few parts per million or less. As these ranges correspond well with the ranges in the two classes of serpentine, it seems safe to conclude that nickel is neither lost nor introduced in the process of serpentinization. It should also be noted that nickel occurs to a lesser extent in nickeloan stevensite, pimelite, talc, and chlorite; these minerals are commonly associated with serpentine minerals.

Chromium, like nickel, is known to be high in ultrabasic rocks, and correspondingly, Class *A* serpentines tend to be higher in this element than those of Class *B*. The range of concentration is, however, much greater than for nickel, and there are two samples of Class *A* serpentines that contain only a few parts per million of chromium. Unlike nickel, which is an integral component of olivine and other major silicate minerals of ultrabasic rocks, chromium is present in the form of the accessory mineral chromite, which may be distributed very erratically in these rocks. Hence the chromium content of an ultrabasic rock could vary greatly from one hand specimen to the next, even from a single body of rock, depending on the amount of chromite that happened to be present in each specimen. The large variation in the chromium content of Class *A* serpentines is, therefore, ascribed to this erratic distribution of chromite in the parent rock rather than to any movement of chromium in or out of the rock during serpentinization. Examples of k ammerite forming through the alteration of chromite have been described (MILLER, 1953), but the close association of the two minerals indicates that chromium does not move any great distance during this reaction. The presence of 0.01% or more of chromium is indicative of Class *A* serpentine.

Cobalt ranges from 0.001 to 0.007% in Class *A* serpentines, except for sample F-40, which it is abnormally low. Among Class *B* serpentines, it is below the limit of detection (0.0005% Co) in nine out of eleven samples and about 0.001% in two samples.

Scandium is known to substitute for magnesium in minerals of the ultrabasic rocks but its content in dolomites and magnesian calcite is extremely low (RANKAMA and SAHAMA, 1950 pp. 516-517). The element was detected only in Class A serpentines.

Copper, titanium, and manganese concentrations in the serpentines are non-diagnostic for determining the genetic class to which a serpentine belongs.

Boron is present in the serpentines, and ranges from 0.0003 to ~~0.015~~ 0.05%. The data suggest that Class B serpentines tend to be richer in this element. SAHAMA (1945) studied the boron content of ultrabasic rocks from Finland and found concentrations in the range of 0.003 to 0.03% boron. He correlated the boron content with the degree of serpentinization of the dunites and concluded that boron was introduced during the serpentinization process. Other observations, such as those of DUPARC and SIGG (1914) on the presence of tourmaline in serpentine-bearing rocks, have also suggested that boron might be associated with ultrabasic rocks. Our studies are not directly comparable with those of SAHAMA, for we did not study the relation of the fresh ultrabasic rocks to altered rocks containing successive increments of serpentine. The question of the relation of boron in the serpentines of Classes A and B to the parent rock is complicated by the occurrence of pegmatites at many localities. The trend for the Class B serpentines to be richer in boron seems to be a true one.

In summary, we have found that the study of the minor elements in serpentines is of diagnostic value in studies on mineral genesis. Class A serpentines may be easily differentiated from Class B serpentines by their concentrations of nickel in excess of 0.01%. Serpentine of Class A also tend to be significantly richer in chromium, cobalt, and scandium. Class B serpentines are richer in boron. In general, the concentrations of the minor elements in serpentines seem merely to reflect the concentrations of their parent rocks. Boron appears to be introduced from external sources. In some rocks, the boron may have been introduced by the fluids which formed the pegmatites associated with the serpentines.

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THE OLIVINE-SPINEL INVERSION IN FAYALITE¹

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Geology

The author has previously described the synthesis under high pressure of a spinel polymorph of fayalite (Ringwood, 1958*a*, *b*). The early work on the transition was essentially of an exploratory nature. It revealed that fayalite was stable at pressures below 30,000 bars in the temperature range 400–600° C., while the spinel was stable above 40,000 bars in the same temperature range. Within the pressure range 30,000–40,000 bars, conflicting results were obtained. These may have been caused by metastability or by insufficient experimental accuracy. In an attempt to resolve the conflict, further runs have been carried out. The position of the transition has been approximately located at 600° C. and 500° C., but the accuracy is not sufficient to provide a reliable slope (dp/dt). It is clear that many additional runs would be required in order to find the slope. Since the author has now ceased working on this problem, it seemed advisable to record the results of runs carried out (Table 1).

Charges were prepared by weighing out ferric oxide, metallic iron powder, and Mallinckrodt silicic acid in the proportions required to give the fayalite composition plus a 10–20% excess of iron. These components were then intimately mixed together by grinding under acetone. The purpose of the excess iron was to maintain oxidized iron in the divalent state. The charges were subjected to the desired temperature and pressure in a "squeezer" apparatus (Griggs and Kennedy, 1956) which was frequently calibrated for temperature and checked for piston distortion.

After completion of a run, temperature and pressure were swiftly lowered. The transition is sluggish and no difficulty was experienced in quenching the high pressure form to atmospheric pressure. Products were examined by x-ray and optical methods. Identification of the spinel form of fayalite was based upon its optical properties and powder pattern, which have been previously described (Ringwood, 1958*b*).

Appearance of the charges under the microscope varied from opaque, indefinite aggregates to completely crystallized, colorless to green masses of fayalite or spinel crystals. The powder patterns showed that the opacity and darkness of samples was due principally to the presence

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TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS

No.	Temperature ° C.	Pressure (bars)	Time of run (hours)	Phases present (a) (b)	Notes
F3	500	20,000	7	magnetite (fayalite?)	
F6	500	20,000	24	fayalite, magnetite	(c)
F11	500	20,000	14	fayalite, (magnetite)	
F14	500	25,000		fayalite, (magnetite)	
F2	500	30,000	16	magnetite, spinel	(e)
F5	500	30,000	24	spinel, magnetite	(c)
F15	500	30,000		fayalite, magnetite	
F16	500	35,000	12	fayalite	
F1	500	40,000	8	spinel, ((magnetite))	
F4	500	40,000	24	spinel, (magnetite)	
F13	600	25,000	3	fayalite, magnetite	
F8	600	30,000	3	fayalite	
F9	600	35,000	3	fayalite	
F10	600	40,000	3	spinel, ((fayalite))	
F12	600	45,000	3	spinel, (magnetite)	
F7	600	45,000	4	spinel	(c)
F17	600	70,000	1	spinel, ((fayalite))	(d)

- (a) In all runs, some unreacted iron remained in the product. This has not been recorded in the above table.
- (b) Phases are recorded in order of abundance. Single brackets denote rarity, double brackets denote extreme rarity.
- (c) In these runs, thermocouple behaved irregularly, preceding a corrosion break. Temperature could have been as much as 20° higher than that recorded.
- (d) Starting charge was moistened Rockport fayalite.
- (e) "Spinel" refers to the spinel polymorph of fayalite.

of magnetite. It was noticed that little or no magnetite was present when the charges had been prepared shortly before using. However if charges had been mixed more than one day, before being run, appreciable quantities of magnetite were likely to be found in the product. This may be due to oxidation of metallic iron in the charge by water from the silicic acid.

From Table 1 it is seen that the position of the transition at 600° C. is close to 38,000 bars. At 500° C. there appears to be a region of indifference where equilibrium is not always attained, with the transition probably between 30,000 and 35,000 bars.

A sample of moistened Rockport fayalite was run at 600° C. and 70,000 bars for one hour. Almost complete conversion to spinel was obtained.

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