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SERPENTINIZATION CONSIDERED AS A CONSTANT VOLUME METASOMATIC PROCESS: A REPLY[1]

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In his discussion of my paper N. J. Page adheres to the belief, expressed by Hostetler, Coleman, Mumpton, and Evans (1966, p. 75), that:

"Extensive brucite formation during serpentinization indicates . . . , unless massive amounts of both magnesia and silica are removed from the ultramafic mass, volume increases of about 40 percent. Field evidence supporting such migration is generally lacking."

In direct contradiction to this belief is my conclusion (p. 707) that:

"The physical evidence leaves little room for argument . . . but that serpentinization is essentially a constant volume metasomatic process which requires removal of about 30 percent by weight of the original bivalent oxides and SiO_2 in peridotite."

[1] Publication authorized by the Director, U. S. Geological Survey.

I discussed chemical data which I believe are consistent with the physical evidence. Page presents additional data on distribution of CaO in ultramafites, but otherwise his discussion impresses me as an expression of the reluctance of the "expansionist" school to admit the validity of the definitive physical evidence, and to accept the geochemical implications. In essence Page argues three main points:

1) During serpentinization there is not much migration of MgO, and "the ratio of CaO to MgO removed is consistently larger than the ratio of these oxides in the original peridotite".
2) My plots of average serpentine compositions from Faust and Fahey (1962, p. 18) are misleading.
3) Failure to distinguish between "the two distinct types of 'alpine' serpentinites" probably results in misleading conclusions about volume relationships.

Page's separate plots of CaO and MgO in serpentinites are a real contribution to the chemistry of ultramafites, but their interpretation involves recognition of some of the difficulties inherent in investigations of serpentinization. Although the two plots of the oxides (Page's Fig. 2) are similar in showing reduced scatter of plotted analyses with the transition from fresh rocks to serpentinites, the reasons for this similarity may differ fundamentally.

Page's Figure 2b, I believe, tells essentially the same story for MgO alone that the upper part of my Figure 1 does for MgO, FeO, and CaO combined. In both figures the vertical spread of oxides plotted is much less in serpentinites containing more than 10 percent H_2O than it is in rocks containing less than 8 percent. In Figure 2b, for example, of 74 serpentinites that contain more than 10 percent H_2O, 54 (73 percent) contain between 33 and about 40 percent MgO, but of 60 "fresh" ultramafites containing less than 5 percent H_2O, only 16 (27 percent) fall in this range. The maximum range of MgO in Page's plot is about 25 percentage points in fresh rocks but only 12 in serpentinites, disregarding the three lowest "stragglers" in each instance. In my Figure 1, the corresponding ranges are about 20 and 11 percentage points, respectively. Page says that:

"Approximately 10 percent of the analyses . . . in figure 2b . . . could form a serpentinite containing a mixture of 10 percent brucite (6.9% MgO) and 90 percent serpentine if fully serpentinized. This is the ratio of brucite to serpentine suggested by Thayer (1966, p. 692)."

I would point out that all 17 of Page's analyses containing at least 0.5 percent more MgO than his serpentine minerals, lie in the theoretical brucite composition field, and are of relatively fresh rocks that contain 5

percent or less H_2O; also none of the serpentinite analyses containing 10 percent or more H_2O falls in his brucite field. I believe that my statement (p. 692), " . . . Very few of the serpentinites plotted contain as much as 5 percent brucite . . . ", applies fully as well to Page's Figure 2b as to my Figure 1. Because dunites and Ca-poor harzburgites undoubtedly are represented abundantly in both groups of rocks, removal of CaO cannot explain the restricted range of MgO in serpentinite analyses, and simple hydration would merely shift the overall scatter pattern downward in proportion to the amount of water added. Figure 2b, I believe, confirms my basic contention that serpentinization is in effect a homogenizing process that produces mixtures of serpentine minerals and magnetite from any ultramafic starting material, and this is consistent with the physical evidence I cited showing that serpentine has replaced olivine and pyroxene at constant volume.

Determination of the chemical behavior of CaO during serpentiniza-tion requires precise modal data which at best might be very difficult to obtain, and in many instances cannot be gotten at all. Because ortho-pyroxenes from ultramafites average less than 1.5 percent CaO and at most contain 2 percent (Hess, 1960, p. 32; Deer, Howie, and Zussman, 1963, p. 16), clinopyroxene must be a significant component of fresh olivine-rich peridotites containing more than 1 percent CaO and of all fresh ultramafites containing more than 2 percent CaO. On the other hand, only about 10 percent of clinopyroxene is required to account for 2 percent CaO (Hess, 1960, p. 36). In Page's Figure 2a the CaO in all but one of the analyses containing more than 8.5 percent H_2O could be ac-counted for by 14 percent or less of relict clinopyroxene, in amounts that would be consistent with the content of H_2O. The absence of analyses containing more than 4 percent CaO and 8 percent H_2O together, in my opinion, probably is attributable to resistance of clinopyroxene-rich rocks to serpentinization rather than to removal of CaO during serpentiniza-tion. Fresh olivine commonly is preserved in rocks containing 25 to 50 percent of clinopyroxene (equivalent to 5 to 10 percent CaO), where ad-joining dunite and harzburgite are completely serpentinized. Comparison of CaO content in Mayagüez peridotites (Hess and Otalora, 1964, p. 157) with Mattson's (1964, p. 17) modal data which are incorporated in my table 2 (p. 689) illustrates the situation. Page's hypothesis requires that CaO begin to move early in the serpentinization process, but usually accessory clinopyroxene finally breaks down only after most or all olivine and orthopyroxene are gone. The modal control for study of possible migration of CaO during serpentinization is not yet available, but for general variation in total bivalent oxides, which I discussed, we have overall modal control: fresh rocks are known to be mixtures of olivine and

pyroxene, and relict features show that the serpentinites cover a similar broad spectrum from dunite to pyroxene-rich rocks.

The use of serpentine mineral compositions from Faust and Fahey (1962, p. 18) is said to be misleading because some of the analyses are of mixtures, despite the fact that practically all serpentinites comprise more than one serpentine mineral. It seems to me that Page's point is significant only as the area of the serpentine-mineral composition field would be changed. Adjustment for modal magnetite in Page's Figure 2b would throw a marked concentration of serpentinite rock analyses upward and to the right into his serpentine-mineral composition field. I cannot, therefore, perceive any important differences in the conclusions to be drawn from my Figures 1 and 4, based on Faust and Fahey's analyses, and Page's Figure 2b based on his analyses of serpentine minerals.

Recognition of two general types of serpentinites derived from alpine ultramafites, Page and I agree, is overdue. The type I called "buckskin-weathering" is composed of "lizardite, chrysotile, and magnetite with or without brucite" according to Page. The verde antique serpentinite probably consists largely of antigorite, with or without brucite, but I would not include talc and magnesite as essential minerals. Though Page implies that the two kinds of serpentinites may involve different spatial relationships, preservation of textures in Pennsylvania chromites which contain mixtures of both kinds of serpentine in the gangue lead me to believe otherwise. In short, I believe that volume relationships during alteration in general are independent of, and cannot be determined from, mineral assemblages, unless they preserve the original framework of a rock.

In closing, I would like to modify the statement in my original conclusion (p. 707) "that serpentinization is essentially a constant volume . . . process" to say that, where the evidence is definitive, serpentinization appears to have involved no significant change in volume, but expansion may occur in other situations. I would add, however, that proof of major volume increase and determination of the amount will be very difficult in alpine peridotites as a class. The stratiform complexes, in which regular layered sequences of fresh rocks can be traced continuously into and through zones of serpentinization, appear to be the most promising subjects for investigation of this vexing problem.

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OPTICAL ABSORPTION SPECTRA OF IRON IN THE ROCK-FORMING SILICATES: A DISCUSSION

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I must raise a strenuous objection to many of the explicit statements and implicit assumptions made by W. B. White and K. L. Keester in their paper "Optical Absorption Spectra of Iron in the Rock Forming Silicates" (1966). Ligand field theory, which is used to explain their data, is a practical and elegant model, but is clearly limited to certain types of spectra. One must not make premature and dogmatic assumptions that any one of several possible models will uniquely explain all the data which will be obtained. Alternative models are often necessary such as molecular orbital theory, exciton theory, and band theory.

For example, White and Keester state "the characteristic colors of transition metal ions in aqueous solution and crystals are due to electronic transitions within the unfilled *d*-orbitals of the ions," and that "the theoretical explanation for these effects in terms of the crystal or ligand field theory (Ballhausen 1962; McClure 1959) is now well established and can be directly applied to the explanation of the iron mineral spectra."

Except for the qualifier "characteristic colors," this statement rules out the possibility of charge transfer spectra which usually must be treated by molecular orbital theory rather than ligand field theory. Even this qualification does not limit the applicability of ligand field theory sufficiently to make such statements even generally true. The characteristic color of the permanganate species has been explained only by molecular orbital theory. Note that Mn^{7+} has a d^0 configuration, thus, no d-d transitions.