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Whole-rock trace element analyses of  
chromite-bearing rocks from the lowermost cyclic unit  
of the Stillwater Complex, Montana

by

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

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## Introduction

The purpose of this report is to make available the large quantity of whole rock trace element chemical analyses which have been obtained for chromite-bearing rocks from a drill core at the base of the Ultramafic zone in the Mountain View area of the Stillwater complex, Montana. These data will be used in various forms in future reports on the petrogenesis of the first cyclic unit in the Ultramafic zone within the Mountain View area. The detailed petrography and mineral chemistry of the rocks as well as interpretations of the data presented in this report will be presented elsewhere. This study is a portion of a larger study on the petrogenesis of chromite deposits in the Stillwater complex.

## Location and General Geology

The Stillwater complex is a layered mafic - ultramafic igneous intrusion, about 6000 m thick at its thickest point, which is exposed along a strike length of about 45 km along the northern front of the Beartooth Mountains in south-central Montana (fig. 1). The age of the complex has been determined at  $2701 \pm 8$  m.y. (DePaolo and Wasserburg, 1979). It intrudes older Precambrian sedimentary rocks and is unconformably overlain by Paleozoic and Mesozoic sedimentary rocks. The complex consists of generally concordant layers of rocks of various lithologies. From the bottom to the top of the complex, these lithologies include mainly norites and orthopyroxenites in the Basal zone, peridotites and bronzitites in the Ultramafic zone, and troctolites, norites, anorthosites, and gabbros in the Banded zone. It is generally thought that the complex formed by fractional crystallization and gravitational settling of crystals in a mafic magma. The complex underwent Precambrian deformation, so that the layers that were originally horizontal are now steeply inclined, with dips ranging from  $45^\circ$  NE to overturned to the south. Detailed reports on the geology of the complex are given by Hess (1960), Jones et al. (1960), Jackson (1961, 1969), Page (1977), Raedeke (1982), and Zientek (1983).

The Ultramafic zone is subdivided into a lower Peridotite member, from which our samples were collected, and an upper Bronzite member. The Peridotite member consists of repetitions of rock types called cyclic units, with the ideal sequence being an olivine cumulate overlain by a bronzite + olivine cumulate, overlain in turn by a bronzite cumulate (Jackson, 1961). In the Mountain View area, Jackson (1968) identified 15 such cyclic units, some of which are incomplete. Chromitite layers of varying thickness occur just above the base of the olivine cumulates in 13 of the cyclic units. The chromitite layers are labeled A through K, with the A being stratigraphically lowest.

The samples analyzed for this report are from the Anaconda Company's drill core #M-16, which is in the Mountain View area (figure 1). Fifty-eight samples were collected, and they include the upper 10 feet of the bronzite cumulate at the top of the Basal zone and the bottom 230 feet of the olivine and bronzite + olivine cumulates in the overlying Ultramafic zone. Chromite is an accessory phase in all of the samples, and a 2 meter-thick chromitite layer with up to 65 modal percent chromite occurs near the top of the interval sampled. This chromitite consists of massive chromite seams interlayered with olivine + chromite cumulates, and it correlates with the B chromitite from other nearby drill core. The drill core stratigraphy and sample locations are shown in figure 2.

The samples were analyzed in order to characterize 1) the transition from the Basal zone to the Ultramafic zone, and 2) the first cyclic unit of the Ultramafic zone and the transition to the second cyclic unit with its enclosed chromitite layer. Detailed characterizations of the trace element geochemistry, petrography, and mineral chemistry of the rocks will ultimately be used to determine mechanisms of formation of cyclic units and enclosed chromite layers in the Stillwater's Ultramafic zone.

#### Analytical Techniques and Results

Quantitative determinations of Co, Cr, Mn, Ni, Ti, V, and Zn were made by direct-current arc spectrography in the following manner. A 100 mg portion of each pulverized (-100 mesh) homogeneous sample was mixed with high purity graphite powder (-200 mesh) and a quartz-sodium carbonate (soda quartz) mixture in proportions suited to the planned spectrographic measurements. Calibration standards and reference materials were also mixed with this graphite-soda quartz mixture in preparation for direct-current (d.c.) arc spectrography. In the analysis process for Co, Cr, Mn, Ni, Ti, and V, a 10 mg quantity of each material-graphite mixture was tamped into the cup of a graphite electrode (Ultra Carbon, type 3170). Each of these electrodes then was placed in an arc stand that supported an opposing pair of electrodes by water-cooled, rhodium-plated holders. A 3.17 mm diameter, pointed cylindrical counter electrode (cathode, Ultra Carbon type 1992) was positioned 4 mm away from the upper edge of the cup electrode (anode). Atomization and excitation of the analyte elements in each sample were produced by a 15 ampere d.c. arc across the 4 mm gap between electrodes. The gap distance was maintained throughout each arcing interval as the tips of the graphite electrodes burned away. Atomic spectra originating from the central 2 mm-high portion of the discharge column (in the gap between electrodes), that was within the solid acceptance angle of a 3.4 m Ebert spectrograph, were recorded on a Kodak III-0 emulsion that was on a 10.2 x 25.4 cm glass substrate. The first order reciprocal linear dispersion of this spectrograph was approximately 0.5 nm/mm. The grating blaze was for 350 nm. Chemical processing of each exposed photoplate was accomplished with a solution of Kodak D-19 developer (3 minutes, 20°C), followed by treatment of the emulsion with acetic acid stop solution (30 s), and Kodak general purpose fixer solution (6 minutes). Each "developed" emulsion then

was washed in flowing tap water for 20 minutes, subjected to a Kodak Photo-flo surfactant solution, drained, and dried under a flow of warm air. Microphotometry of spectral lines from exposures of an iron arc made through a 2-step neutral density filter that was positioned at the entrance slit of the spectrograph enabled necessary emulsion calibrations. Seventeen iron lines in the first-order spectral region from 315.7 to 324.8 nm were used for emulsion calibration. The spectral lines measured to establish analytical calibration functions and to determine concentrations of individual elements were: Ti (I) 315.225, Mn (I) 325.614, Cr (I) 301.371, V (II) 310.230, Co (I) 344.917, and Ni (I) 310.188 nm. Relative standard deviations for such spectrographic determinations typically are  $\pm 10\%$ . Details for this analytical approach can be found in descriptions of the d.c. arc spectrographic method by Bastron, et al. (1). The determination of Zn was accomplished by measurements on the Zn (I) 334.502 nm line in spectra produced by a fractional volatilization procedure. This procedure makes use of a sodium carbonate buffer and a 25 ampere arc in an argon atmosphere, and is described by Ansell (2). Again, the relative standard deviation for measured concentrations is  $\pm 10\%$ .

The determination of Pt, Pd, and Rh were made by the fire assay separation, graphite-furnace atomic absorption (A.A.) technique. For this technique, 10 grams of finely-ground sample (-100 mesh) are fused with a flux consisting of PbO, Na<sub>2</sub>CO<sub>3</sub>, borax glass and baking flour. A 2 mg gold wire is added to the mixture. This mixture of sample flux and gold wire is fused at 1000°C for approximately one hour until a melt of two phases, liquid borosilicate slag and a liquid lead phase, is formed. This permits the separation of the noble metals from the slag as lead alloys. Subsequently lead is separated at controlled temperatures in porous bone ash vessels called cupels. The gold bead remaining at the end of cupellation contains Pt, Pd, and Rh. The gold bead is dissolved in aqua regia and is taken to dryness and brought up to 1 ml in 1:1 HCl. The Pt, Pd, and Rh are determined by the graphite furnace A.A. technique. The detection limit for Pt is 1 part per billion (ppb), and for Pd and Rh, it is 0.5 ppb. For further discussions of the technique see Beamish (1966), and Haffety et al. (1977).

Results of the analyses are shown in Table 1. In general, the amounts of Cr, Ti, V, and Zn are related to the amounts of oxides in the rocks, whereas the Co, Pt, Pd, Rh, and in most samples Ni, are related to the amount of accessory sulfides. Mn abundances do not correlate with mineralogy. The Cr, Ti, V, and Zn reach their highest concentrations in chromitite samples. Throughout the core, the Cr concentration shows direct correlation with chromite mode, because chromite is the only mineral in the rocks that accomodates significant amounts of Cr. An increase in Ti concentration in sample 436.5 correlates with increased rutile and ilmenite. The largest jump in Ni and Co contents are in sample 237.2, which contains more sulfides than samples above and below. Increased sulfide mode is also reflected in increases in Pt, Pd and Rh in sample 434, which is at the contact of the Basal and Ultramafic zones. The Pt, Pd, and Rh reach their highest concentrations in the chromitite, probably because of an increase in microscopic platinum group element-bearing sulfide inclusions in chromite grains.

## References

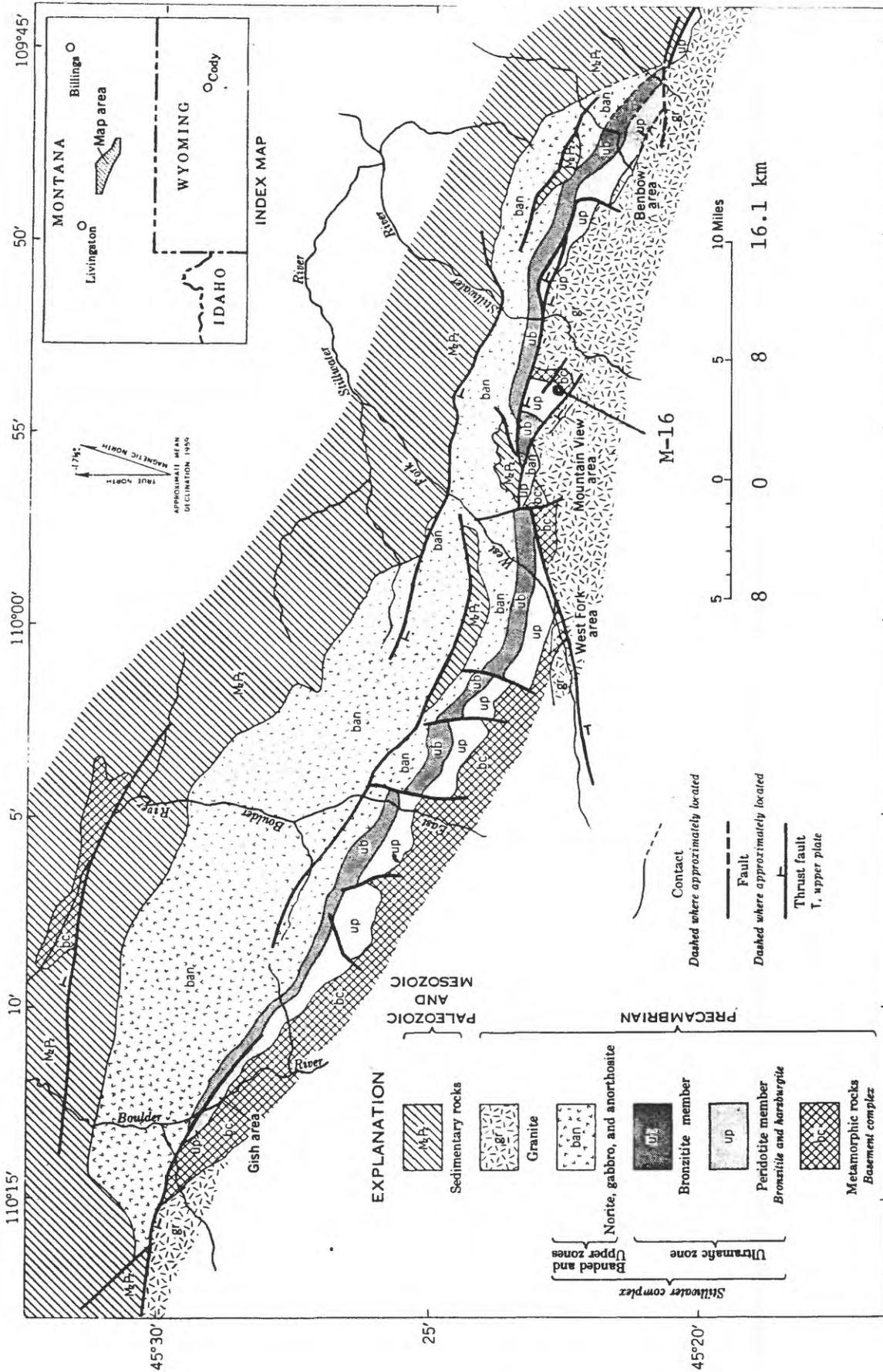
- Annell, C. S., 1967, Spectrographic determination of volatile elements in silicates and carbonates of geologic interest using an argon d.c. arc: in Geological Survey Research 1967, U.S. Geological Survey Professional Paper 575-C, p. C132-C136.
- Bastron, Harry, Barnett, P. R., and Murata, K. J., 1960, Method for the quantitative spectrochemical analysis of rocks, minerals, ores, and other materials by a powder d.c. arc technique: U.S. Geological Survey Bulletin 1084-G, p. 165-182.
- Beamish, F. E., 1966, The analytical chemistry of the noble metals: New York, Pergamon Press, 609 p.
- DePaolo, D. J., and Wasserburg, G. J., 1979, Sm-Nd age of the Stillwater Complex and the mantle evolution curve for neodymium: *Geochimica et Cosmochimica Acta*, v. 43, p. 999-1008.
- Haffty, J. Riley, L. B., and Goss, W. D., 1977, A manual on fire assaying and determination of the noble metals in geological materials: U.S. Geological Survey Bulletin 1445, 58 p.
- Hess, H. H., 1960, Stillwater igneous complex, Montana -- a Quantitative Mineralogical Study: Geological Society of America Memoir 80, 230 p.
- Jackson, E. D., 1961, Primary textures and mineral associations in the ultramafic zone of the Stillwater Complex, Montana: U.S. Geological Survey Professional Paper 358, 106 p.
- \_\_\_\_\_, 1968, The chromite deposits of the Stillwater complex, Montana: p. 1496-1510, in Ridge J. D., ed., Ore deposits of the United States 1933-1967, v. 2, American Institute of Mining, Metallurgical and Petroleum Engineers.
- \_\_\_\_\_, 1969, Chemical variation in coexisting chromite and olivine in chromitite zones of the Stillwater Complex: Economic Geology Monograph 4, p. 41-71.
- Page, N. J., 1977, Stillwater Complex, Montana: Rock succession, metamorphism, and structure of the complex and adjacent rocks: U.S. Geological Survey Professional Paper 999, 79 p.
- Raedeke, L., 1982, Petrogenesis of the Stillwater complex: Seattle, Washington, University of Washington, Ph.D. Thesis, 212 p.
- Zientek, M. L., 1983, Petrogenesis of the Basal zone of the Stillwater complex, Montana: Palo Alto, California, Stanford University, Ph.D. Thesis, 229 p.

Table 1.-- Whole rock trace element analyses [All analyses are in parts per million; \* = not determined; < = below detection limit; analyses of Cr, Ni, Co, Ti, V, Mn, and Z performed by S. Berman; analyses of Pt, Pd, and Rh performed by H. Smith]

Sample Number	Cr	Ni	Co	Ti	V	Mn	Zn	Pt	Pd	Rh
192.1	3300	1600	140	170	180	750	390	*	*	*
196	2400	1200	83	64	68	1300	130	<	<	0.0006
199	2700	1900	92	80	89	1600	99	*	*	*
209	2200	1300	110	100	84	1000	73	0.0028	0.0041	0.0010
215.5	2300	1400	120	110	88	1200	64	*	*	*
220	2500	1500	120	110	92	2000	68	0.0035	0.0045	0.0045
223	1800	1500	130	83	70	1300	51	*	*	*
225	3800	1300	120	82	100	1000	88	0.0041	0.0093	0.0031
226.5	140000	1400	160	150	260	1400	100	0.073	0.46	0.025
227	140000	1800	210	180	340	1500	150	0.038	0.48	0.0040
227.3	28000	1600	190	570	1300	2200	210	0.044	0.17	0.0086
228	19000	1800	160	460	550	1200	200	0.040	0.32	0.015
228.5	41000	1300	220	990	1400	2400	650	0.19	0.74	0.069
228.75	42000	970	210	920	1300	2500	610	0.11	0.36	0.052
229	25000	1300	130	420	560	1400	820	0.058	0.43	0.030
229.5	2800	1900	120	100	82	1200	67	0.066	0.022	0.0033
230	24000	1900	170	490	760	1500	260	0.092	0.46	0.055
231.5	36000	1200	220	760	1200	1900	620	0.042	0.10	0.044
232	2500	1800	100	80	68	1200	110	*	*	*
237.2	2100	3800	440	57	68	2200	360	0.015	0.14	0.0026
242.5	2100	980	97	110	150	2000	100	*	*	*
246	3000	800	84	86	110	1600	81	0.0011	0.0014	0.0006
250	2000	860	82	93	120	1600	94	*	*	*
255.8	2500	870	95	89	150	1800	91	0.0093	0.014	<
257	1100	1700	150	130	92	1400	75	*	*	*
260	2200	980	95	110	140	1700	100	0.0040	0.0088	<
264	2300	890	97	98	120	1500	84	*	*	*
266	1900	2100	130	120	160	1700	110	0.018	0.029	0.0012
268.5	2000	1800	140	140	160	1700	88	*	*	*

Table 1--continued.

270	1800	1200	110	96	110	1400	79	<	<	0.0007
274.2	1700	1800	130	78	98	1400	82	*	*	*
284	1700	2000	140	80	94	1500	90	0.0064	0.012	0.0041
289	2000	2400	150	90	120	1600	88	*	*	*
299	1700	2400	160	76	90	1400	100	<	0.0010	0.0005
306	1700	2200	150	86	110	1700	93	*	*	*
313	1500	2400	150	96	110	2100	110	0.0010	0.0020	<
318	1700	3200	180	150	140	2000	130	*	*	*
328	1700	2300	150	67	85	1900	100	0.0021	0.0041	<
334	1700	3000	160	78	98	1900	100	*	*	*
341	1500	1700	110	42	56	1600	100	0.0018	0.0022	<
353	1800	2700	170	100	130	1900	130	*	*	*
358	1100	2500	150	65	67	2200	120	0.0018	0.0017	0.0006
368	1900	2400	150	110	140	1800	120	*	*	*
373	2000	2100	180	63	120	2000	120	0.0017	0.0039	0.0005
381	2200	1900	180	180	170	1800	140	*	*	*
388	2000	1900	160	150	180	2300	130	0.001	<	0.0006
393.9	1900	1800	140	58	90	1500	140	*	*	*
401	2200	1900	180	80	130	1700	120	0.0015	0.0042	<
408	2000	1600	140	70	110	1600	110	*	*	*
415	1800	1700	150	68	150	2000	180	0.0021	0.0039	<
422.5	2100	1900	160	74	120	1600	160	*	*	*
430	2500	1900	160	180	170	1500	120	0.0028	0.0087	<
432.4	3200	2500	170	160	200	1500	130	*	*	*
434	1900	2100	120	140	140	1300	88	0.14	0.22	0.044
436.5	2000	620	77	410	200	2000	80	*	*	*
440	1900	550	75	130	150	1800	78	0.001	<	<
445	1900	480	71	220	180	1800	70	*	*	*
450	2200	630	88	200	220	1900	81	0.0021	0.0052	0.0005



Simplified from Jones, Peoples, and Howland, 1960

From Jackson, 1961

FIGURE 1.—Geologic index map of the Stillwater complex. The Basal zone is too thin to be shown at this scale.

M-16 DRILL CORE

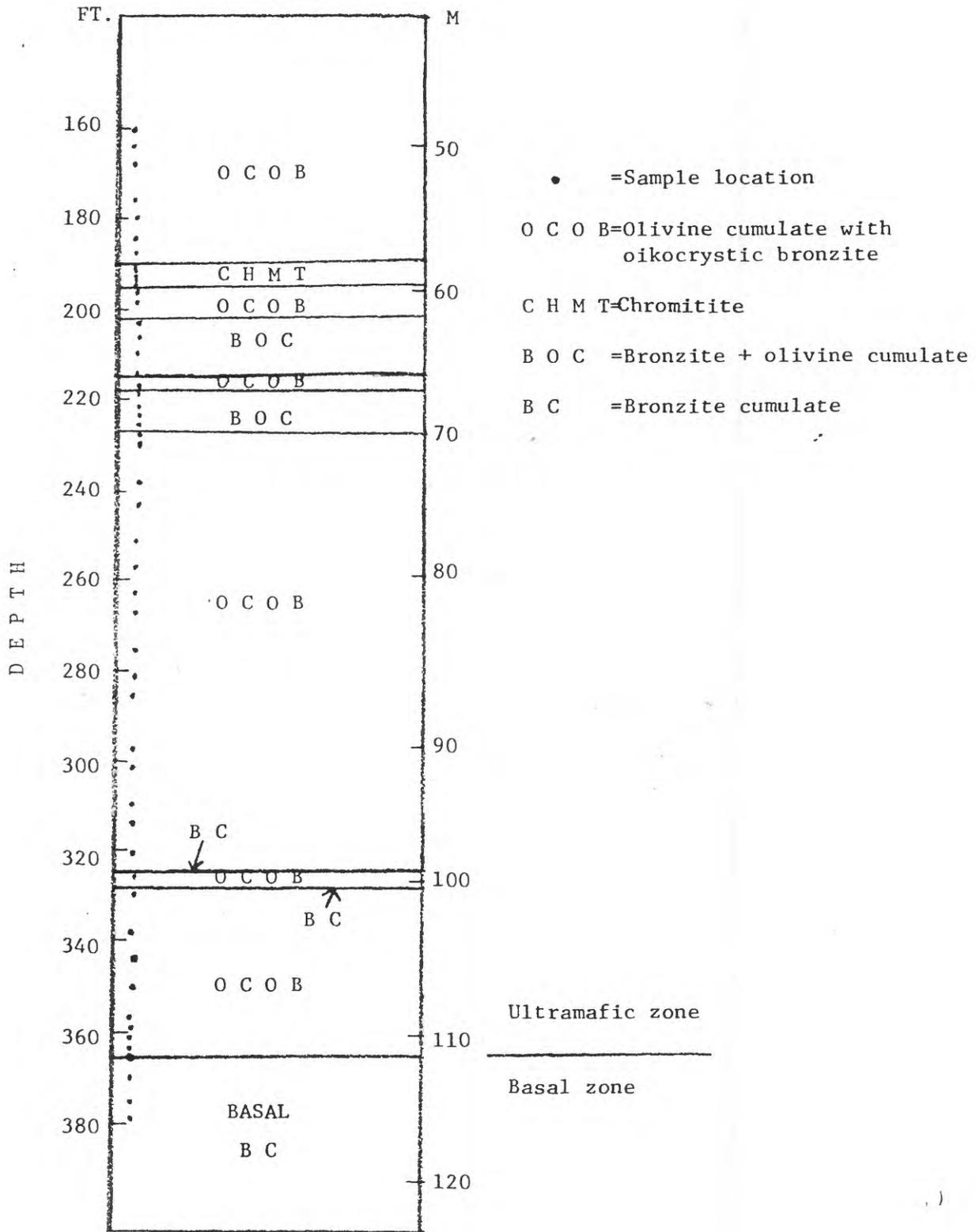


Figure 2. M-16 drill core stratigraphy and sample locations.