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Alteration of Chromite from the Twin Sisters Dunite, Washington

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Abstract

Chromite in the Twin Sisters dunite, an alpine-type ultramafic body some 90 km², occurs as minor disseminated euhedral-subhedral crystals or in clusters forming pods and lenses. Modal proportions of chromite in the pods and lenses are frequently as high as 80 percent. Ferritchromite occurs as rims on chromite crystals that are bordered by chlorite and (where still available) olivine.

Microprobe analyses of chromite, ferritchromite, chrome-magnetite, olivine, and chlorite show that the chromite-ferritchromite boundary is sharp (less than 10 microns) and that, relative to chromite, ferritchromite is enriched in Cr, Fe, Ni, and Mn and impoverished in Mg and Al. However, when chrome-magnetite, found only in association with serpentine, is the alteration product, there is a marked decrease in chromium.

Chromite alteration appears to take place above the upper stability limit of serpentine and below that of chlorite.

Introduction

Alteration of chromite to opaque highly reflecting borders has been reported by several authors (Weiser, 1967; Kern, 1968; Mihálik and Saager, 1968; Beeson and Jackson, 1969; Frisch, 1971). Because the alteration product is rich in iron, it has been called "gray magnetite" (Horninger, 1941) or "ferritchromit" (Spangenberg, 1943). Several quantitative chemical descriptions of this alteration product have been worked out (Table 1). Most workers, however, investigated only the distribution of the major elements between the chromite and its alteration product. In this investigation, the behavior of four major elements (Mg, Fe, Al, and Cr) and also six minor elements (Ni, Mn, Co, Ti, Zn, and V) were studied.

Beeson and Jackson (1969) reported that chromite alteration accompanies the change of associated olivine and orthopyroxene to chlorite. Many of the reported instances of chromite alteration have been related to serpentinization perhaps caused by late pneumatolytic-hydrothermal solutions (Kern, 1968). From a fresh dunite nodule from a basaltic tuff, Frisch (1971) reported chromite alteration that appears to have resulted from high-temperature, late-magmatic processes prior to eruption.

Two types of chromite alteration were recognized in this study. In one, the alteration product is chrome-bearing magnetite which is associated with serpentine. In the other, the alteration product is ferritchromite which is in no way associated with serpentine. Serpentine associated with the magnetite was not studied in detail.

Petrography

Chromite crystals in the Twin Sisters dunite (Ragan, 1967) occur either as disseminated, euhedral-to-subhedral grains which constitute less than 1 percent of the rock, or as concentrations in bands or schlieren. They also occur in clusters forming pods and lenses some 0.3 meters or more thick. These pods and lenses are distributed irregularly over the entire rock body. Modal proportions of chromite in these pods and lenses are frequently as high as 80 percent. The chromite crystals in the pods and lenses are characteristically anhedral and some display granulated margins. The dominant, although restricted, change in the original chromite pods and lenses is the breakdown of chromite plus olivine and enstatite to ferritchromite and chlorite.

The chromite alteration product in three specimens from chromite lenses from locations 2, 5, and 7 (Figure 2, Onyeagocha, 1973) were studied in detail. Several chromite crystals with well developed ferritchromite rims were studied, but data are presented

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for only a few that illustrate the extent and nature of this alteration. These samples consist of unaltered chromite and olivine with local zones of ferritchromite and light purple chlorite. The chromite grains are anhedral to subhedral. Chlorite is kinked, representing an adjustment to forces exerted by the surrounding chromite during chlorite growth. There is some textural intergrowth of ferritchromite and chlorite (identified as chlorite by partial microprobe analysis) much like that shown by Golding and Bayliss (1968, p. 174, Figure 8) which they called "coarsely pitted altered chromite."

At the boundary between a chromite lens and dunite, chromite alteration did not yield ferritchromite but instead chrome-bearing magnetite and books of kinked green chlorite. The magnetite is associated with serpentine. Instead of the increase in Cr observed in the other samples, the alteration product shows a tremendous decrease in Cr. The lower Cr content noted in magnetite relative to ferritchromite is accompanied by a lower Cr content of coexisting, green chlorite relative to the purple chlorite.

Discussion

Microprobe analyses of phases associated with chromite alteration (Table 2) show that olivine is particularly homogeneous. No grain-to-grain-variations were observed, nor did step scans across individual grains reveal any inhomogeneity. Unaltered chromite in these specimens exhibits no variations that could not be accounted for by count statistics. Ferritchromite and chrome-bearing magnetite showed slight inhomogeneity. Cr, Fe, and Al in chlorite are remarkably variable within grains and from grain to grain. Within a single grain the Cr-content increases toward the unaltered chromite core and decreases towards olivine. For example, specimen 5-5A (near chromite) has 3.2 percent Cr_2O_3 whereas 5-5B (near olivine) only contains 0.10 percent Cr_2O_3 (Table 2).

Figure 1 shows step scans across a crystal in which the chromite-ferritchromite boundary is sharp (less than 10 microns). The scans also show that, relative to the chromite, ferritchromite is enriched in Cr, Fe, Ni, and Mn, and impoverished in Mg and Al. The pattern is not clear for Co, Zn, and V.

TABLE 1. Pattern of Chromite Alteration

No Pattern	Enriched in Chromite	Enriched in Ferritchromite
	Al, Mg	Fe, Cr (Weiser, Case I, 1967)
	Al, Mg, Cr	Fe (Weiser, Case II, 1967)
Al, Mg, Cr		Fe (Mihalik & Saager, 1968)
	Al, Mg. Cr	Fe (Beeson & Jackson, 1969)
Cr	Al, Mg	Fe (Lapham, 1964)
	Al	Fe (White, 1966)
	Cr	Fe (Muir & Tilley, 1964)
	Cr, Al, Mg, Zn	Fe, Ti, Ni (Frisch, 1971)
	Al, Mg	Fe, Cr, Ni, Mn, Co, Ti, Zn, V (This study)
	Cr, Al, Mg	Fe, Co, Zn, Ni (Enriched in magnetite) (This study)

The decrease in the ratios, $Mg/(Mg + Fe^{2+})$ and $Al/(Cr + Al + Fe^{3+})$, and the simultaneous increase in $Fe^{3+}/(Cr + Al + Fe^{3+})$ observed in both types of chromite alteration according to Jackson (1969), indicates that the chromite formed at high temperature and later re-equilibrated at lower temperature. This is corroborated by the data in Table 3 for chrome-bearing magnetite where apparent equilibration temperatures, for what they are worth, are negative. No difference in temperature is apparent between olivine-chromite and olivine-ferritchromite in this study (Table 3) nor did Frisch (1971) notice any difference. Since the olivine is, in general, homogeneous, an alternate interpretation of re-equilibration with olivine richer in iron is not applicable here. In fact, judging from the equation written for alteration of chromite to ferritchromite using the actual analytical data obtained in this study, it appears that the initial olivine is richer in iron. The equation[2] assumes that Al, Cr, and Mg were conserved.

$$\begin{aligned}
&\underset{\text{chromite}}{4.44(Mg_{0.72}Fe^{2+}{}_{0.29})(Cr_{1.16}Al_{0.75}Fe^{3+}{}_{0.09})\,O_4}\\
&+\ \underset{\text{olivine}}{3.52(Mg_{1.81}Fe^{2+}{}_{0.19}SiO_4)}\\
&+\ \underset{\text{enstatite}}{2.54(Mg_{0.91}Fe^{2+}{}_{0.09}SiO_3)} + 8\ H_2O + 0.27\ O_2\\
&=\ \underset{\text{ferritchromite}}{3(Mg_{0.55}Fe^{2+}{}_{0.45})(Cr_{1.57}Al_{0.08}Fe^{3+}{}_{0.35})\,O_4}\\
&+\ \underset{\text{chlorite}}{(Mg_{10.22}Cr_{0.43}Al_{1.17}Fe^{2+}{}_{0.19})(Si_{6.06}Al_{1.94})\,O_{20}\,OH_{16}}
\end{aligned}$$

Excess Fe and Si were partitioned to form forsterite and enstatite with the same Fe/Mg ratio. Written in this manner, the equation shows that only H_2O and O_2 need be introduced. The alteration, therefore, appears to be a response to changing oxygen fugacity (Irvine, 1965) and changing f_{H_2O}.

A volume-for-volume replacement of the outcrop as postulated by Beeson and Jackson (1969, p. 1096)

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[2] In writing this equation, specimen 2-4A#1 was used for chromite, ferritchromite, and chlorite. No olivine was found within several cm of this crystal. Olivine used in the equation is from specimen 2-4 and is some 10 cm away from 2-4A.

TABLE 2. Electron Microprobe Analyses of Chromite, Ferritchromite, Magnetite, Olivine, and Chlorite from the Twin Sisters Dunite, Washington

	CHROMITE									FERRITCHROMITE			MAGNETITE			
	2-4	2-4A#1	2-4A#2	5-4B	5-4C	5-4D	5-5	5-5D	5-7	2-4A#1	2-4A#2	5-5	5-4A	5-4B	5-4C	5-7
TiO_2	0.03	0.05	0.05	0.10	0.13	0.08	0.08	0.08	0.05	0.12	0.90	0.13	0.02	0.03	0.02	0.02
Al_2O_3	21.3	20.6	21.1	11.7	10.7	16.6	17.5	16.8	18.1	1.8	2.7	9.9	0.48	0.57	0.67	0.56
Cr_2O_3	47.0	47.7	46.5	51.5	52.7	47.1	51.1	50.8	50.4	56.0	54.9	55.5	0.07	0.25	1.9	4.2
Fe_2O_3*	3.8	3.7	4.0	9.7	10.4	6.8	4.1	4.6	3.9	13.1	13.0	7.9	69.5	69.6	67.7	64.9
FeO*	11.0	11.3	10.8	13.9	13.7	17.9	12.4	13.6	12.6	14.7	13.7	14.1	25.3	25.5	26.4	27.2
MnO	0.23	0.24	0.41	0.50	0.58	0.52	0.44	0.47	0.4	0.47	0.63	0.55	0.22	0.18	0.18	0.45
MgO	15.5	15.2	15.4	12.6	12.8	10.3	14.3	13.4	14.2	10.1	11.5	12.4	2.4	2.4	2.0	1.7
CoO	0.04	0.03	0.04	0.08	0.11	0.11	0.07	0.08	0.05	0.04	0.08	0.10	0.25	0.23	0.22	0.21
ZnO	0.05	0.07	0.03	0.14	0.14	0.27	0.05	0.08	0.05	0.20	0.14	0.10	0.29	0.29	0.23	0.24
NiO	0.10	0.10	0.09	0.11	0.15	0.09	0.08	0.09	0.09	0.49	0.34	0.13	1.4	1.5	1.4	0.60
V_2O_3	0.11	0.12	0.12	0.16	0.19	0.21	0.16	0.18	0.12	0.16	0.16	0.19	0.05	0.07	0.04	0.13
Total	99.16	99.11	98.54	100.49	101.60	99.98	100.28	100.18	99.99	97.18	98.05	101.00	99.93	100.62	100.76	100.21
IONIC PROPORTIONS ON THE BASIS OF 32 OXYGEN ATOMS																
Ti	.006	.009	.009	.019	.025	.015	.015	.015	.009	.026	.187	.025	.005	.007	.005	.005
Al	6.156	5.982	6.137	3.554	3.231	5.032	5.129	4.972	5.309	.600	.880	3.019	.171	.202	.237	.200
Cr	9.112	9.292	9.074	10.496	10.676	9.579	10.047	10.085	9.916	12.530	12.000	11.354	.017	.059	.451	1.004
Fe^{3+}	.699	.684	.747	1.878	2.004	1.315	.762	.877	.732	2.782	2.711	1.538	15.791	15.709	15.294	14.756
Fe^{2+}	2.256	2.339	2.227	3.003	2.931	3.861	2.583	2.851	2.614	3.490	3.179	3.056	6.402	6.406	6.623	6.873
Mn	.048	.050	.086	.109	.126	.113	.093	.100	.091	.113	.148	.121	.056	.046	.046	.115
Mg	5.665	5.582	5.665	4.841	4.888	3.949	5.301	5.015	5.267	4.260	4.739	4.782	1.080	1.073	.894	.766
Co	.008	.006	.008	.017	.023	.023	.014	.016	.010	.009	.018	.021	.061	.055	.053	.051
Zn	.009	.013	.005	.027	.026	.051	.009	.015	.009	.042	.029	.019	.065	.064	.051	0.54
Ni	.020	.020	.018	.023	.031	.019	.016	.018	.018	.112	.076	.027	.340	.362	.338	.146
V	.022	.024	.024	.033	.039	.043	.032	.036	.024	.036	.035	.039	.012	.017	.010	.032

	OLIVINE			
	2-4	5-4	5-5	5-5 chl
SiO_2	41.4	41.2	41.4	41.7
FeO	4.4	8.2	5.7	5.1
MnO	0.05	0.13	0.10	0.08
MgO	53.1	50.7	52.4	52.6
NiO	0.71	0.43	0.52	0.62
CaO	0.00	0.01	0.01	0.01
Total	99.66	100.67	100.13	100.11
Ionic proportions on the basis of 4 oxygen atoms				
Si	.996	.997	.996	1.001
Fe	.089	.166	.115	.102
Mn	.001	.003	.002	.002
Mg	1.904	1.829	1.880	1.882
Ni	.014	.008	.010	.012
Ca	.000	.000	.000	.000
R^{2+}	2.008	2.006	2.007	1.998

	CHLORITE						
	2-4	2-4A#1	2-4A#2	5-4	5-5A	5-5B	5-7
SiO_2	33.4	32.3	33.1	31.4	32.1	33.0	31.4
Al_2O_3	13.5	14.1	14.5	15.8	15.4	16.2	17.0
Cr_2O_3	0.66	2.9	1.8	0.01	3.2	0.10	0.46
FeO	1.5	1.2	1.3	2.3	1.5	1.7	1.8
MnO	0.03	0.04	0.04	0.01	0.02	0.01	0.01
MgO	37.0	36.9	36.4	37.2	35.8	36.8	36.5
NiO	0.21	0.24	0.30	0.24	0.36	0.34	0.16
Total	86.30	87.68	87.44	86.85	88.38	88.15	87.33
Ionic proportions on the basis of 28 oxygen atoms							
Si	6.317	6.062	6.196	5.928	5.986	6.107	5.883
Al^{IV}	1.683	1.938	1.804	2.072	2.014	1.893	2.117
Al^{VI}	1.326	1.181	1.395	1.443	1.371	1.640	1.637
Cr	.099	.430	.266	.001	.472	.015	.068
Fe	.237	.188	.204	.363	.234	.263	.282
Mn	.005	.006	.006	.002	.003	.002	.002
Mg	10.430	10.322	10.156	10.468	9.951	10.150	10.193
Ni	.032	.036	.045	.036	.054	.051	.024

*FeO and Fe_2O_3 computed from total iron assuming perfect spinel stoichiometry.

for the Stillwater alteration is not necessarily applicable to this study. There are no continuous beds or bands recognizable in the Twin Sisters dunite, but the bending and kinking of some chlorite crystals represent growth in a confined environment and therefore are an expression of increase in volume. The same phenomenon is known to occur in mica formation (Misch, 1936) and in periclase dehydration (Burnham, 1959; Turner and Weiss, 1965; Carpenter, 1967).

It should be emphasized that the chromite alteration observed in some lenses is restricted to only small fractions of the total lens. Specimens collected a few centimeters away from the alteration do not exhibit

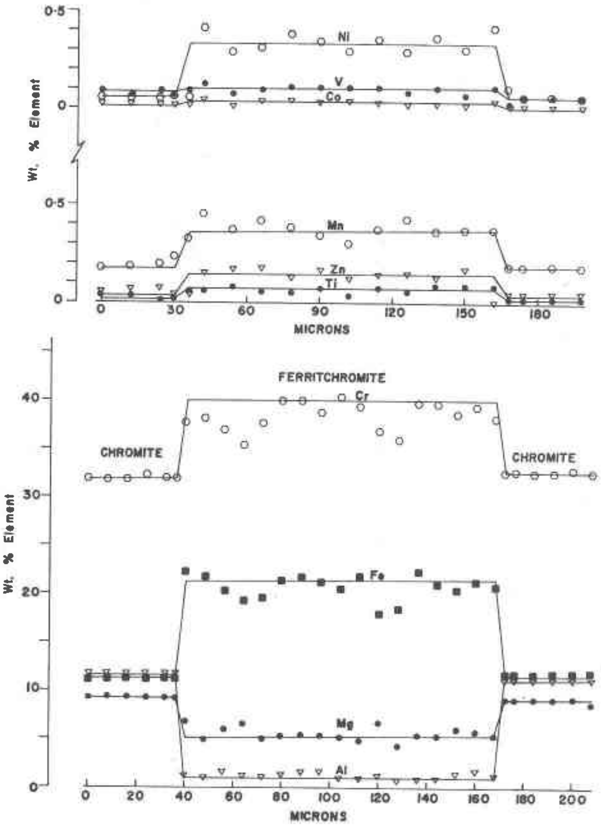

FIG. 1. Step scans across altered chromite.

TABLE 3. Derivation of Apparent Equilibration Temperature, Using the Equation of Jackson (1969)*

Specimen	Mg/Mg+Fe	Mg/Mg+Fe	α	β	δ	$K_{D_{Mg\text{-}Fe^{2+}}}$	T°C
Olivine-Chromite							
	Olivine	Chromite					
2-4	.955	.715	.571	.386	.044	8.45	1154
2-4A#1	.955	.705	.582	.375	.043	8.89	1138
2-4A#2	.955	.718	.569	.385	.047	8.34	1163
5-4B	.917	.617	.659	.223	.118	6.85	1660
5-4C	.917	.625	.671	.203	.126	6.62	1756
5-4D	.917	.506	.602	.316	.083	10.80	1090
5-5	.949	.672	.630	.322	.048	9.07	1210
5-5D	.942	.638	.633	.312	.055	9.23	1212
Olivine-Ferritchromite							
	Olivine	Ferritchromite					
2-4A#1	.955	.550	.787	.038	.175	17.39	1188
2-4A#2	.955	.599	.770	.056	.174	14.24	1298
5-5	.949	.610	.714	.190	.097	11.89	1225
Olivine-Magnetite							
	Olivine	Chrome-magnetite					
5-4A	.917	.144	.001	.011	.988	65.47	-85
5-4B	.917	.144	.004	.013	.984	65.93	-81
5-4C	.917	.119	.028	.015	.957	81.81	-62

* This equation (Jackson, 1969, p. 63, equation 9) reads

$$T = \frac{5580\alpha + 1018\beta - 1720\delta + 2400}{0.90\alpha + 2.56\beta - 3.08\delta - 1.47 + 1.987 \ln K_{D_{Mg\text{-}Fe^{2+}}}}$$

where α, β, and δ--as cited in the above table--are the fractions of trivalent cations, Cr, Al, Fe^{3+} respectively, in spinel; and where $\alpha + \beta + \delta = 1.0$

$$K_{D_{Mg\text{-}Fe^{2+}}} = \frac{\{Mg/(Mg + Fe^{2+})\}^{ol}\ \{Fe^{2+}/(Mg + Fe^{2+})\}^{chr}}{\{Fe^{2+}/(Mg + Fe^{2+})\}^{ol}\ \{Mg/(Mg + Fe^{2+})\}^{chr}}$$

any alteration at all. The alteration characteristically is concentrated in the chromite-rich rocks whereas chromite and olivine in the adjacent dunite are unaltered. It would thus appear that the alteration occurs above the upper stability limit of serpentine but below that of chlorite. Frost (1973) has shown that in progressive metamorphism of serpentinite, magnetite co-exists with serpentine. With increase in grade, the oxide becomes richer in chrome until chromite is formed. This change in composition of the spinel phase is at least partially related to the coexisting phyllosilicate. Using the data of Kitahara, Takenouchi, and Kennedy (1966), the upper stability of serpentine at 10 kbar water pressure would yield temperatures of about 570°C. Using the data of Fawcett and Yoder (1966), the upper limit of chlorite is around 800°C. The 570°C to 800°C temperature interval is wide enough for all metamorphic reactions in the Twin Sisters dunite reported in Onyeagocha (1973).

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