

Chlorites from granitic rocks of the central Sierra Nevada batholith, California¹

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SUMMARY. Occurrence and major- and minor-element compositions of chlorites from plutonic rocks of the central Sierra Nevada batholith have been studied in detail.

Chlorite has formed largely as an alteration product of biotite, presumably late in the magmatic history of the granitic rocks as a result of subsolidus reaction. Major-element composition of chlorite is strongly influenced by composition of coexisting biotite. Minor-element differences between the two minerals can, for the most part, be attributed to structural differences. The minor-element data, particularly for Cu, indicate that the process of chloritization is not a likely mechanism for release of ore metals from primary minerals.

CHLORITE is a common, though admittedly minor, constituent of calc-alkaline plutonic rocks; however, there have been few studies of the mineral in these rocks. As part of a continuing mineralogical and geochemical study, the occurrence and composition of chlorites from granitic rocks of the central Sierra Nevada batholith have been investigated. Earlier reports describing the mineralogy of the same rocks include papers on hornblendes (Dodge *et al.*, 1968) and biotites (Dodge *et al.*, 1969) among others. The geology of the region from which samples were collected has been reviewed in numerous publications by P. C. Bateman and his colleagues (e.g. Bateman *et al.*, 1963; Bateman and Wahrhaftig, 1966).

Occurrence and origin of chlorite. In plutonic rocks of the Sierra Nevada batholith chlorite tends either to be interlaminated with biotite or to occur as discrete, small grains disseminated throughout the host rock. Rarely does chlorite form pseudomorphs with minerals other than biotite. Small granules of anhedral epidote and sphene are frequently associated with chlorite, particularly when it occurs with biotite. The occurrence of small granules of potassium feldspar in proximity to chlorite, an association pointed out by Chayes (1955), has been noted but is not common. In contrast, biotite in rocks that do not contain potassium feldspar is almost never chloritized; otherwise, chlorite is distributed throughout plutonic rocks of the batholith regardless of rock composition, age, or other geologic controls.

The amount of chlorite in the batholithic rocks is extremely variable but usually is less than 2 per cent by volume of the host rock. The percentage of chlorite to the total of chlorite plus biotite averages about 10 but ranges from 0 to over 90.

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There is no change in amount of chlorite with depth in drill cores from 300- to 600-metre-deep boreholes (Lachenbruch, 1968) in the Sierra Nevada; that is, there is no quantitative increase of the mineral in rocks exposed at the surface. The presence of chlorite throughout these cores eliminates the possibility that chloritization in these rocks could in any way be related to weathering phenomena, a view held by Evernden and Kistler (1970, p. 6). Furthermore, X-ray diffraction photographs of all chlorites analysed chemically for major elements in this study clearly show that the minerals are *I1b* polytypes and therefore of high-temperature origin (Brown and Bailey, 1962; Hayes, 1970). Presumably, the chlorites formed late in the magmatic history of their host rocks, probably as a result of deuteric action.

Composition of chlorite. Those chlorites selected for compositional study were purified as carefully as practicable by repeatedly centrifuging crushed, washed rock powders in heavy liquids and by then passing concentrates through an electromagnetic separator. Partly chloritized biotite, the principal contaminant, could not be completely extracted. Final sample purity varied considerably but was appreciably less than 95 % in only three samples (FD-3, BP-2, and FD-12) and was estimated to exceed 98 % in several samples.

Only limited data on optical and physical properties of the analysed chlorites have been determined (table I). Optic axial angles of all chlorites are 0° or near 0° . In agreement with observations of previous workers (e.g. Orcel, 1927; Hutton, 1940; Albee, 1962), the optic sign changes at $(\beta + \gamma)/2$ about 1.629 , and chlorites with an index on the low side of the sign change generally have abnormal brown interference colours, whereas those on the high side generally have abnormal blue or violet interference colours. All chlorites have the pleochroic scheme $\alpha < \beta = \gamma$, where α = very pale yellow and $\beta = \gamma$ = green.

Major-element compositions of seven chlorites are given in table II. Because amounts of some of the purified chlorites were limited (less than 500 mg), the compositions of four samples (FD-3, BCc-12, MT-2, I-397) were determined partly by emission spectrometry. The other three were analysed by conventional wet chemical techniques.

Analyses were calculated on the basis of 36 (O,OH,F) per formula unit according to the general chlorite formula $Y_{12}Z_8O_{20}(OH,F)_{16}$, where *Y* represents octahedrally coordinated cations and *Z* tetrahedrally coordinated cations. Following the practice of Deer *et al.* (1962), for analyses where only total H_2O has been determined this figure has been used for calculating formulae; otherwise, only H_2O+ has been included.

Compositionally, the chlorites span the oxidized and unoxidized series defined by Hey (1954), although there is no relation between high Fe_2O_3 content and low H_2O+ values, which indicates that ferric iron is probably primary and not a product of oxidation (Deer *et al.*, 1962, p. 147). Thus a classification scheme such as that proposed by Foster (1962) seems more appropriate than Hey's. The chlorites fall into either the ripidolite or brunsvigite fields defined by Foster.

Minor-element contents of 13 chlorites, which were quantitatively estimated using emission spectrographic methods described by Bastron *et al.* (1960), are given in table I.

TABLE I. *Optical properties, specific gravities, and minor element contents of chlorites from granitic rocks of the Sierra Nevada batholith*

	FD-3	MT-1	BP-2	FD-12	FD-20	SL-32	SL-18	BCc-13	MT-2	BCc-12	HL-4	I-397	FD-15
<i>Optical properties and specific gravities</i>													
$(\beta + \gamma)/2^*$	1.619	1.629	1.629	1.645	1.641	1.629	1.633	1.629	1.623	1.617	1.627	1.623	1.621
Sign	+	+	—	—	—	—	—	—	+	+	+	+	+
Int. col.†	brown	brown	—	blue-black	blue	violet	violet	violet-blue	brown	brown	violet-brown	brownish-violet	brown
Sp. gr.‡	2.82	2.92	2.92	2.90	3.06	2.98	3.02	2.92	2.92	2.80	2.98	2.98	2.90
<i>Minor elements§ (weight per cent)</i>													
Ba	0.0085	0.0033	0.026	0.0085	0.0033	0.0036	0.0044	0.0044	0.0055	0.0032	0.0044	0.0038	0.0043
Ca	0.45	0.22	0.15	0.085	0.14	0.17	0.24	0.30	0.26	0.20	0.20	0.14	0.20
Co	0.0075	0.0030	0.0055	0.0026	0.0020	0.0045	0.0050	0.0060	0.0085	0.0090	0.0050	0.0055	0.0085
Cr	0.0007	0.0008	0.0019	< 0.0004	0.0008	0.0055	0.0040	0.0055	0.0055	0.0036	0.0007	0.0013	0.0018
Cu	0.0095	0.0095	0.023	0.020	0.0070	0.014	0.0085	0.010	0.013	0.014	0.012	0.0080	0.010
Ga	0.0085	0.0030	0.0044	0.0060	0.0050	0.0040	0.0040	0.0030	0.0050	0.0085	0.0055	0.0080	0.0050
Mn	2.0	1.3	0.44	1.4	0.70	0.80	0.55	0.44	0.80	1.1	0.90	2.0	0.80
Nb	< 0.002	< 0.002	< 0.002	0.014	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Ni	0.0050	0.0012	0.0038	0.0011	0.0010	0.0028	0.0028	0.0042	0.0055	0.0060	0.0015	0.0015	0.0048
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.008	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Sc	< 0.0004	< 0.0004	0.0013	0.0080	0.0026	0.0008	< 0.0004	< 0.0004	< 0.0004	< 0.0004	0.0018	0.0020	< 0.0004
Sr	< 0.0002	< 0.0002	0.0070	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002
Ti	0.50	0.13	0.60	0.48	0.10	0.10	0.20	0.18	0.20	0.11	0.17	0.17	0.095
V	0.017	0.018	0.020	0.0065	0.0070	0.021	0.024	0.027	0.026	0.033	0.022	0.015	0.017
Zr	< 0.002	< 0.002	0.014	0.009	0.006	< 0.002	< 0.002	< 0.002	< 0.002	0.004	< 0.002	0.007	< 0.002

* Refractive index values are ± 0.002 ; measurements made with N_{Dj} light.

† Interference colour.

‡ Specific gravity, ± 0.05 .

§ Elements present in amounts less than the following detectability levels: Ag, 0.0002; As, 0.1; Au, 0.006; B, 0.002; Bi, 0.002; Cd, 0.01; Ce, 0.04; Ge, 0.002; Hf, 0.06; Hg, 0.02; In, 0.002; Ir, 0.02; La, 0.006; Mo, 0.001; Os, 0.0004; Pb, 0.002; Pt, 0.002; Re, 0.01; Rh, 0.0006; Ru, 0.2; Ta, 0.08; Te, 0.2; Th, 0.1; Ti, 0.01; U, 0.1; W, 0.1; Y, 0.002; Yb, 0.0002; Zn, 0.01.
Elements determined by spectrographic methods by R. E. Mays.

Chemistry of the process of chloritization. Major-element composition of chlorite appears to be strongly influenced by composition of coexisting biotite; this relation is shown in fig. 1 by comparison of relative amounts of Fe³⁺, Fe²⁺, and Mg in five pairs of the two minerals. Chlorite consistently contains less total iron relative to

TABLE II. *Analyses of chlorites from granitic rocks in the Sierra Nevada batholith*

Sample number	FD-3	MT-1	FD-20	BCC-12	MT-2	FD-15	I-397	
<i>Major elements (weight per cent)</i>								
SiO ₂	29*	27.06	24.68	28*	27*	27.36	27*	
Al ₂ O ₃	18.2*	19.55	20.92	20.0*	19.5*	19.03	20.0*	
Fe ₂ O ₃	4.0	6.78	3.11	3.9	5.4	2.49	3.7	
FeO	17.01	17.92	28.84	17.56	18.09	20.16	18.67	
MnO	1.84*	1.24	0.77	0.84*	0.96*	0.90	1.49*	
MgO	17.3*	15.58	10.16	18.3*	16.5*	17.63	15.9*	
CaO	0.91*	0.36	0.16	0.43*	0.44*	0.18	0.37*	
Na ₂ O	0.13	0.07	0.03	0.12	0.04	0.06	0.09	
K ₂ O	0.71	0.25	0.09	0.15	0.37	0.10	0.30	
H ₂ O ⁺	} 10.6	{ 10.98	11.20	} 11.5	12.1	{ 11.18	} 11.2	
H ₂ O ⁻								0.14
TiO ₂	0.90*	0.23	0.17	0.15*	0.35*	0.12	0.32*	
P ₂ O ₅	< 0.01	—	—	< 0.01	< 0.01	—	< 0.01	
F	0.35	0.09	0.06	0.08	0.10	0.12	0.31	
O : F	0.15	0.04	0.03	0.03	0.04	0.05	0.13	
	101	100.21	100.29	101	101	99.57	99	
<i>Atomic ratios to 36 (O, OH, F)</i>								
Si	} Z	5.96	5.62	5.30	5.67	5.49	5.61	
Al ^{IV}		2.04	2.33	2.70	2.33	2.51	2.31	2.39
Al ^{VI}		2.37	2.41	2.59	2.44	2.17	2.36	2.52
Fe ³⁺	} Y	0.62	1.06	0.50	0.59	0.83	0.39	0.58
Ti		0.14	0.04	0.03	0.02	0.05	0.02	0.05
Mg		5.30	4.82	3.25	5.52	5.01	5.47	4.93
Fe ²⁺		2.93	3.11	5.18	2.97	3.08	3.51	3.25
Mn		0.32	0.22	0.14	0.14	0.17	0.16	0.26
Ca		0.20	0.08	0.04	0.09	0.10	0.04	0.08
Na		0.05	0.03	0.01	0.05	0.02	0.02	0.04
K		0.19	0.07	0.02	0.04	0.10	0.03	0.08
OH		14.54	15.21	16.03	15.53	16.43	15.51	15.54
F		0.23	0.06	0.04	0.05	0.06	0.08	0.20
Total Y	12.12	11.84	11.76	11.86	11.53	12.00	11.79	

Analysis of FD-3, BCC-12, MT-2, and I-397 by N. H. Suhr and of MT-1 and FD-20, by S. T. Neil.

* Value determined by emission spectrometry.

magnesium, and iron tends to be slightly, though probably not significantly, more oxidized than in biotite. Nevertheless, there is close, systematic, compositional correspondence between the two minerals. Distribution ratios of selected minor elements for 12 coexisting biotite-chlorite pairs are given in table III (minor-element data for 11 of the biotites are given in Dodge *et al.*, 1969, data for the other one—sample

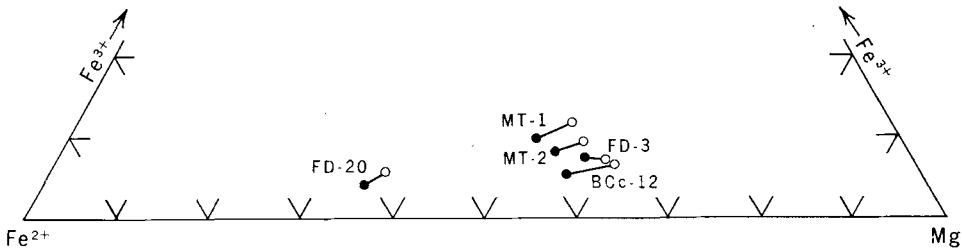


FIG. 1. Relation of Fe^{+3} - Fe^{+2} -Mg contents of coexisting chlorites and biotites in granitic rocks from the central Sierra Nevada batholith. Chlorites are represented by open circles, biotites by filled circles. Biotite compositions are from Dodge *et al.* (1969).

TABLE III. *Distribution coefficients of selected minor elements in twelve coexisting chlorites and biotites*

	Ba	Co	Cr	Cu	Ga	Ni	V
Kd. average	0.07	1.33	1.03	1.78	1.23	1.70	0.67
Kd. range	0.02-0.25	0.82-1.80	0.56-2.09	0.79-3.51	0.83-1.89	0.80-2.65	0.39-1.19

$Kd = (X_{\text{chlorite}}/X_{\text{biotite}})$, where X = concentration of a specific element in g/cm^3 .

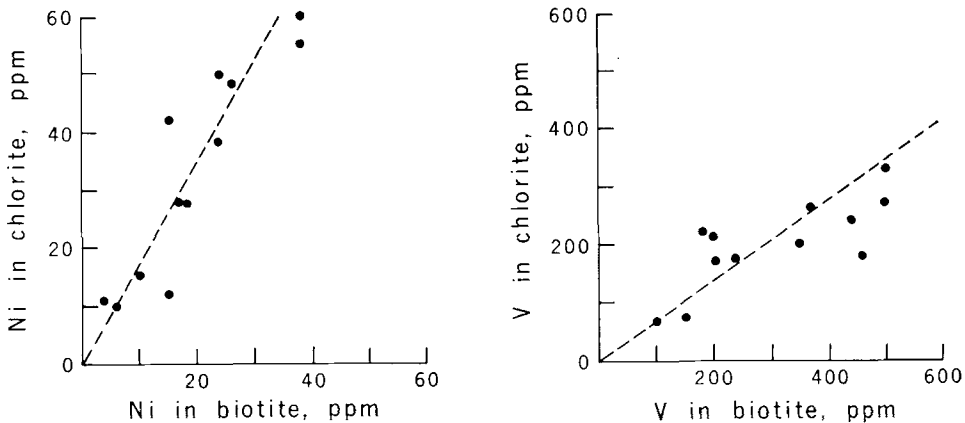


FIG. 2. Distribution of Ni and V between coexisting chlorite and biotite. The dashed line represents the mean distribution coefficient for the respective element.

FD-15—are unpublished), and the distribution of two of the minor elements V and Ni is depicted in fig. 2. Other elements show similar distribution patterns but generally with slightly more scatter. Much of the scatter may be attributable to analytical uncertainties. Partition data are generally at least approximately concordant, suggesting an equilibrium distribution of the minor elements between the two mineral phases.

Derivation of chlorite from biotite appears to have taken place with no volume change. On a constant volume basis, that is, with respect to a specific volume of biotite relative to an equal volume of coexisting chlorite, decrease of Si, Na, K, Ti, F, Ba, and V and increase of Al, total Fe, Mg, Mn, Co, Cu, Ni, perhaps Ga, and, of course, H₂O, have taken place by chloritization of biotite. Ca and Cr show no consistent trend of depletion or enrichment. Major-element changes and consequent reactions involved during the process of chloritization of biotite have been discussed by Chayes (1955) and McNamara (1966). As with major elements, minor-element changes can in part be attributed to structural differences between the two minerals. A specific volume of chlorite has about one-third less tetrahedral sites and about 50 per cent more octahedral sites than an equal volume of biotite, and chlorite has no specific sites available for twelve-coordinated large cations. Thus Ba and Na, both substituting for the large, 12 coordinated cation K, are depleted, whereas Mn, Co, Cu, Ni, and Ga, substituting for major elements in octahedral sites, are generally concentrated in chlorite relative to biotite. Enrichment of Ti and V in biotite is puzzling, for both elements presumably are in octahedral sites. Nickel (1954) also noted that these elements have a higher content in biotite than in chlorite. He suggested that even though Ti⁴⁺ and V⁴⁺ have electronegativities similar to iron, and on this basis might be expected to behave in a manner similar to iron, they in fact both have a high valence and may be less readily taken up by chlorite. The mineral contains a rather high proportion of trivalent Al in octahedral coordination, and addition of these elements could cause a localized net charge imbalance. In chlorite, an excess of charges in the 'brucite' layer is probably balanced by a deficiency of charges in tetrahedral sites of the 'talc' or silicate layer. Reluctance of the chlorite structure to accept Ti is reflected by the close association of sphene with chlorite in Sierra Nevada granitic rocks.

Conclusions. Chlorite has formed late in the magmatic history of the granitic rocks of the Sierra Nevada batholith, commonly as an alteration product of biotite. Composition of chlorite is closely related to composition of associated biotite; the close correspondence of relative ferric and ferrous iron contents in the two minerals suggests that they formed under similar oxidation conditions. Oxygen fugacities of late-stage magmatic fluids were likely governed by compositions of primary ferro-magnesian minerals.

Trace-element contents of chlorites and coexisting biotites indicate that the process of chloritization is not a likely mechanism for release of ore metals from primary minerals. In fact, chlorite is apparently a concentrator of some of the minor elements, including copper, of granitic rocks.

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