Canadian Mineralogist
Vol. 26, pp. 413-422 (1988)

CHLORITE–CALCITE AND CORRENSITE–DOLOMITE CRYSTALLIZATION DURING TWO SUPERIMPOSED EVENTS OF HYDROTHERMAL ALTERATION IN THE "LES CRÊTES" GRANITE, VOSGES, FRANCE

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ABSTRACT

Petrographic observations show that the "Les Crêtes" Paleozoic granite (Vosges, France) has been altered by two successive hydrothermal events that superimposed their effects either in vein deposits or in massive rock. The first event was a propylitic-type alteration that induced precipitation of calcite + chlorite. Biotite was strongly affected by chloritization near large carbonate veins, whereas amphibole was replaced slightly along internal microfissures. Chemical compositions of chlorite are dependent upon local equilibria, except along walls of carbonate veins corroded by a vermicular iron-rich chlorite. Effects of the second hydrothermal event are observed around the largest subvertical calcite veins; these were reopened and sealed by secondary precipitation of dolomite + hematite. Corrensite corroded the walls of the calcite veins and replaced amphibole, but chlorite and primary biotite were unaffected. The main difference between the two alteration events is the presence of hematite, which indicates that redox $f(O_2)$ conditions changed, whereas pH and $P(CO_2)$ were relatively stable. There is no petrological evidence of a temperature decrease: both of the parageneses are stable between 120 and 280°C. The change in redox conditions probably arose from the reopening of the large subvertical calcite veins, which allowed infiltration of meteoric water into the system. The corrensite cannot be considered to be a transitional step in the conversion of saponite to chlorite, as occurs in active geothermal fields and in diagenetic environments; instead, the mineral is an independently formed phase.

Keywords: chlorite, corrensite, hydrothermal alteration, granite, Vosges, France.

SOMMAIRE

Les observations pétrographiques montrent que le granite des Crêtes (Vosges, France) est altéré en deux épisodes hydrothermaux qui superposent leurs effets aussi bien dans les dépôts minéraux des veines que dans la roche altérée. Le premier s'apparente à une altération de type propylitique caractérisée par calcite + chlorite. La biotite est intensément chloritisée à proximité des veines à carbonates, alors que l'amphibole n'est que très légèrement altérée le long de microfissures. La composition chimique de la chlorite reflète les équilibres locaux, sauf le long des veines à carbonates, qui sont corrodés par de la chlorite vermiculaire riche en fer. Le second épisode hydrothermal a été observé autour des veines à calcite subverticales, qui ont été réouvertes et scellées par un dépôt de dolomite + hématite. La corrensite cristallise le long des bords de la veine à calcite et remplace totalement l'amphibole. La chlorite et la biotite primaire ne sont pas affectées. La différence majeure entre les deux épisodes d'altération est marquée par la présence d'hématite, qui indique que la fugacité d'oxygène a changé alors que pH et P (CO$_2$) sont restés approximativement constants. Il n'y a aucune évidence pétrologique d'une diminution de température, et les paragenèses sont stables entre 120 et 280°C. Le changement des conditions d'oxydo-réduction est probablement lié à la réouverture des veines à calcite subverticales qui a provoqué l'infiltration d'eau météorique dans le système. Ceci montre que la corrensite, dans ce cas, ne peut être considérée comme une phase transitoire de la réaction saponite → chlorite, comme c'est le cas dans les champs géothermiques actifs ou dans les environnements diagénétiques. Elle se comporte comme une phase indépendante.

Mots clés: chlorite, corrensite, altération hydrothermale, granite, Vosges, France.

INTRODUCTION

Chlorite and corrensite have been observed frequently in sedimentary rocks and in hydrothermally altered basalts, hyaloclastites and granites (Brigatti & Poppi 1984, Velde 1985). In most of these occurrences corrensite is considered to be an intermediate step in the reaction saponite → chlorite. The regularly interstratified 50% chlorite - 50% saponite crystallizes in a wide range of P,T conditions (Inoue *et al.* 1984, Inoue 1985). This phase frequently is associated with zeolites and illite–smectite mixed-layer minerals. The reverse reaction, *i.e.*. chlorite → corrensite → saponite or vermiculite, is known in weathering processes of basic or ultrabasic rocks (Herbillon & Makumbi 1975, Proust 1983). Dilute solutions percolate through soils or weathering profiles and destabilize the chlorite component by leaching of Mg^{2+} and Fe^{2+} ions and by oxidation of the remaining Fe^{2+} (Proust *et al.* 1986). Expandable layers appear (saponite or vermiculite), first in a regularly interstratified mode with chloritic layers. In upper horizons of soils or weathering profiles, they replace all of the chloritic layers.

Correnside thus appears to be a necessary intermediate step in the reaction of chlorite to a trioctahedral expandable clay-mineral, either in diagenetic or weathering processes. If this is true, the question is raised as to which direction the reaction proceeds

TABLE 1. AVERAGE CHEMICAL COMPOSITIONS OF PRIMARY BIOTITE[1] AND AMPHIBOLE[2]

	Si	Al	Fe^{2+}	Mg	Ti	Mn	Ca	Na	K	$\frac{Fe}{Fe+Mg}$
Biotite[1]	2.78	1.25	1.04	1.63	0.22	0.01	0.01	0.04	0.85	0.39
S.D.*	0.08	0.04	0.15	0.08	0.03	0.01	0.01	0.04	0.08	0.02
Amphibole[2]	7.48	0.60	1.38	3.60	0.07	0.03	1.79	0.33	0.08	0.28
S.D.*	0.07	0.05	0.04	0.07	0.02	0.01	0.06	0.02	0.04	0.02

[1] based on 15 microprobe analyses. [2] based on 20 microprobe analyses
* S.D. : standard deviation.

A Cameca MS 46 microprobe equipped with a Si-Li Ortec detector was used. The analytical conditions are the following : 15 kV, 1.10^{-3} µA, spot diameter : 3 µm, counting time 120 s, standards orthoclase, albite, diaspore, wollastonite, periclase, quartz, hematite, rutile, pyrolusite.

The data are recast on a $O_{10}(OH)_2$ basis for biotite and $O_{22}(OH)_2$ for amphibole. Fe is assumed to be divalent.

when corrensite coexists with chlorite. If, on the contrary, corrensite is an independent mineral phase, then the problem is to determine the physicochemical conditions that control its stability (or metastability) with respect to chlorite.

The "Les Crêtes" granite (Vosges, France) was affected by hydrothermal alteration which produced secondary corrensite and chlorite in veins and in the wallrocks. These phases are associated with carbonates. The aim of our study was to determine through petrographic observations whether or not corrensite and chlorite crystallized together, or successively, during a single hydrothermal event. The first alternative implies that corrensite is an intermediate step in the transformation to chlorite, whereas crystallization during two distinct alteration events suggests that corrensite is an independent phase.

GEOLOGICAL SETTING

The Vosges Massif is an intrusive complex in which the "Les Crêtes" granite represents the Dinantian intrusive episode (Gagny 1969). This granitic body is characterized by a microporphyritic texture; some orthoclase phenocrysts attain 3 cm. Several mylonitized bands, 1 to 30 mm thick, were observed in the drill cores. Based on an examination of 12 drill-core samples, the modal composition of the rock is quartz 23.2%, K–Na-feldspar 24.2%, plagioclase 20.6%, biotite 20.2%, amphibole 11.8%. Amphibole crystals are euhedral (0.8–2 mm across); locally, some are replaced by a late magmatic quartz + feldspar assemblage. The composition of the amphibole corresponds to the magnesian actinolite domain (Leake 1978). Biotite also is Mg-rich, and is typically euhedral. The average chemical compositions of the primary Mg–Fe phases are given in Table 1. K-feldspar crystallized as large, typically zoned euhedra of orthoclase, and as microcline in xenomorphic perthitic grains in which the amount of albite varies from 15 to 45%. Optical determinations of orthoclase and microcline were controlled by X-ray diffraction [position and intensities of the (131) and (1$\bar{3}$1) peaks]. Plagioclase grains are always euhedral, and vary in composition from An_{28} to An_{34}.

TABLE 2. MACROSCOPICAL ASPECT OF THE SAMPLES STUDIED IN THE DRILL-CORE OF "LES CRETES" GRANITE.

Samples	Depth	Rock alteration type	Veins
1	0 m	Chloritized	–
2	– 4,10 m	Strongly weathered Mylonite band (3 mm thick)	Open fractures with iron oxides
3	– 6,70 m	Chloritized	Carbonate + chlorite
4	– 7.00 m	Chloritized	Open fractures with iron oxides
5	– 12.30 m	Slightly chloritized	–
6	– 14.30 m	Chloritized	–
7	– 15.30 m	Fresh biotite	Carbonate + corrensite
8	– 16.00 m	Fresh biotite	Carbonate + corrensite
9	– 17.00 m	Chloritized Mylonite band (1 mm thick)	Carbonate + chlorite + corrensite
10	– 18.30 m	Chloritized Mylonite bands (1 mm thick)	Carbonate + chlorite
11	– 22.00 m	Fresh biotite	Carbonate + corrensite
12	– 25.00 m	Slightly chloritized	–

Numerous mm-wide carbonate + chlorite or carbonate + corrensite veinlets crosscut the granite in the upper part of the drill core. All veinlets are subvertical and are bordered by wallrock alteration halos 2 to 5 mm wide. Twelve samples were taken from the upper 25 m, both in the porphyritic facies and in the mylonitized zones (Table 2).

ANALYTICAL METHODS

Bulk X-ray diffraction was performed on powders and oriented preparations of the >2 µm fraction of each sample. Alteration phases were identified by X-ray diffraction analysis of material extracted from thin sections using the "micropicking" technique (Beaufort *et al.* 1983). A Philips PW 1730 diffractometer with an Elphyse position-sensitive detector was used; operating conditions were 40 kV, 40 mA, and Co$K\alpha$ radiation.

Electron-microprobe analysis conditions were those recommended by Velde (1984). Compositions are expressed in atomic proportions calculated on an $O_{10}(OH)_2$ basis for micas, $O_{10}(OH)_8$ for chlorite and corrensite, and $O_{22}(OH)_2$ for amphiboles. Total iron is arbitrarily considered to be Fe^{2+}, even for corrensite which contains appreciable amounts of Fe^{3+} (Brigatti & Poppi 1984).

RESULTS

Two types of alteration features can be seen macroscopically in the twelve samples: 1) wallrock alteration around carbonate + chlorite or corrensite veins; 2) selective pervasive alteration (Titley 1983), in which the initial microtexture of the rock is preserved, even in mylonitized zones. The upper part of the drill cores (10 m) has been affected by weathering, and open fractures are coated by iron oxides.

Alteration halos along veins

The "Les Crêtes" granite is cross-cut by straight veins, 2–3 mm wide, interconnected by a network of sinuous hairline veinlets (50–200 μm across). Intergranular joints and intracrystalline microcracks in primary minerals are filled by secondary minerals. Four types of veins or veinlets can be distinguished by their mineralogical assemblages: 1) chlorite + calcite + dolomite + hematite; 2) corrensite + dolomite + calcite + hematite; 3) chlorite + corrensite + dolomite + calcite + hematite, and 4) calcite.

The *chlorite–carbonate–hematite veins* are zoned: a thin red layer, 10–20 μm wide, of hematite mixed with dolomite outlines the contact between the dolomitic zone (100–200 μm wide) and the vermicular chlorite (Fig. 1). Large crystals (100–200 μm) of calcite are broken approximately in their middle and are sealed by dolomite associated with hematite. Vermicular chlorite, which has invaded the wallrock to a distance of 3–4 mm, appears along intergranular joints or intracrystalline microcracks in all of the primary minerals of the granite. In these areas, biotite is strongly chloritized and amphibole is partly replaced by chlorite and calcite.

The *corrensite–carbonate–hematite veins* are filled by dolomite + hematite where vein widths are less than 0.8 mm, or by calcite on the walls and dolomite–hematite in the center where vein widths are greater than 0.8 mm. The wallrocks are corroded by corrensite, which has invaded microcracks to a distance of 1 mm from the carbonate veins. Amphibole grains in this area have been replaced extensively by corrensite and dolomite. Biotite and chlorite are not altered.

The *chlorite–corrensite–carbonate–hematite veins* (800 μm width) are zoned: calcite was deposited on the edges of the fractures, and dolomite + hematite in the centers. The calcite crystals are broken, suggesting that dolomite precipitated after reopening of the veins. Quartz and plagioclase in wallrock up to 800 μm from the veins are strongly corroded by a mixture of vermicular chlorite and corrensite.

The *calcite veins* are invariably narrow (50 μm maximum). They were observed in all of the samples in which a pervasive chloritization has affected biotite and amphibole.

Pervasive alteration

Features of pervasive alteration are widely distributed throughout the drillhole. The main characteristics are the replacement of ferromagnesian primary minerals (biotite and amphibole) and plagioclase by secondary products. Quartz and K-feldspar seem unaffected. The rock microtexture is well preserved even in mylonitic zones.

FIG. 1. Drawing of a chlorite–dolomite–hematite vein from sample number 9. Ch: vermicular chlorite, d: dolomite, o: Fe-oxide (hematite), pl: plagioclase, q: quartz.

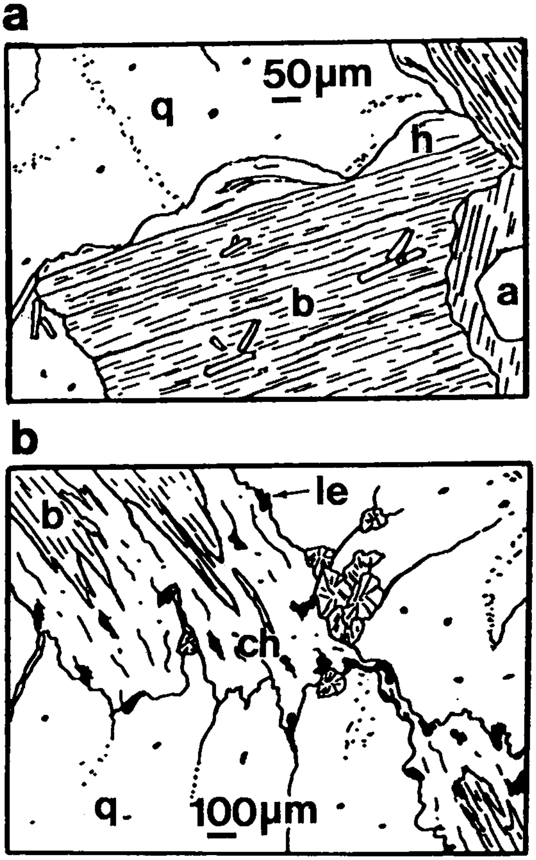

FIG. 2. a. Chlorite growths (ch) on (001) faces of biotite (b) in contact with a crystal of quartz (q). FIG.b. Replacement of biotite (b) by chlorite (ch) and leucoxene (le). Secondary microfissures radiate from the biotite crystal inside quartz (q). Spherulites of chlorite crystallized along intergranular or intracrystalline microfissures.

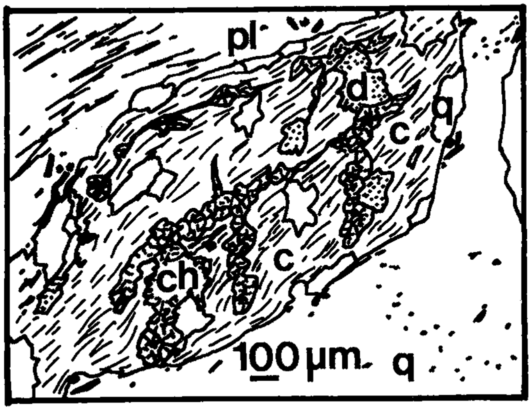

FIG. 3. Spherulitic chlorite (ch) in amphibole microcracks. The amphibole relicts are replaced by corrensite (c) and dolomite (d). q: quartz, pl: plagioclase.

Biotite is partly to completely replaced by chlorite except in samples 7, 8 and 11 (Table 2) in which some unaltered crystals are observed even near corrensite veinlets. In these samples the early stages of the chloritization process are detectable along the (001) biotite faces in contact with quartz. Round growths of chlorite (20–50 µm) are similar to those described in other hydrothermal occurrences (Beaufort 1981, Meunier & Proust 1982, Parneix *et al.* 1985). In some cases the chlorite is associated with very small grains of leucoxene (Fig. 2). Chloritization proceeded as a replacement that broadly preserved the micaceous structure. Small grains of leucoxene rim the chloritized parts. Where the extent of replacement of the initial biotite exceeds 50%, the shape of the mica flake is no longer preserved and the chloritic material has invaded all of the neighboring quartz and plagioclase crystals. Secondary microcracks are filled by chlorite + titanite around the chloritized areas.

TABLE 3. CHEMICAL COMPOSITION OF CHLORITE*

Si	Al	Fe^{2+}	Mg	Ti	Mn	Ca	Na	K	$\frac{Fe}{Fe+Mg}$
In biotite									
2.96	2.12	1.90	2.98	-	-	0.02	-	-	0.39
2.89	2.23	1.71	3.13	-	0.03	0.01	-	0.01	0.36
2.81	2.39	1.50	3.26	-	0.01	0.02	-	0.01	0.32
2.87	2.02	1.84	3.26	0.02	-	0.01	-	0.04	0.36
2.91	2.26	1.65	3.09	-	0.02	0.03	-	-	0.35
2.93	2.23	1.74	3.01	-	0.03	0.01	-	0.01	0.37
2.96	2.28	1.58	3.03	0.01	0.01	0.01	0.01	0.01	0.34
2.91	2.34	1.71	2.89	0.01	0.04	0.01	-	-	0.37
2.91	2.28	1.72	3.00	-	0.01	0.01	-	0.02	0.36
2.92	2.26	1.52	3.20	0.01	-	0.02	-	0.02	0.32
2.75	2.49	1.53	3.16	0.01	0.01	0.01	-	0.01	0.37
2.75	2.45	1.69	3.04	0.01	0.03	0.02	-	0.01	0.36
2.85	2.22	1.76	3.10	0.01	0.03	0.02	-	0.01	0.36
2.94	2.25	1.56	3.07	0.03	0.01	0.01	0.01	0.03	0.34
Average composition									
2.88	2.27	1.67	3.09	0.01	0.02	0.02	0.02	0.01	0.35
Standard deviation									
0.07	0.12	0.12	0.11	0.01	0.01	0.01	0.04	0.01	0.02
In amphibole									
2.95	2.19	1.40	3.35	-	0.04	0.01	-	0.01	0.29
3.04	1.91	1.47	3.51	-	0.02	-	-	0.01	0.29
2.96	2.12	1.64	3.16	-	0.04	-	-	0.02	0.34
2.97	2.21	1.71	2.94	0.02	0.03	-	-	0.02	0.37
3.05	1.92	1.56	3.33	-	0.05	0.02	-	0.02	0.32
3.10	1.87	1.17	3.78	-	0.01	0.03	-	0.01	0.24
2.95	2.19	1.40	3.35	-	0.04	0.01	0.02	0.01	0.30
3.10	1.87	1.17	3.78	-	0.01	0.03	-	0.01	0.24
Average composition									
3.02	2.03	1.44	3.40	-	0.03	0.01	0.03	0.01	0.30
Standard deviation									
0.07	0.16	0.20	0.29	0.01	0.02	0.01	0.02	0.01	0.02
In fissures									
2.93	2.30	1.64	3.00	-	0.02	0.02	-	-	0.35
2.69	2.60	1.98	2.69	0.01	0.04	0.01	-	-	0.42
3.00	2.09	1.37	3.42	0.01	0.02	0.03	0.02	-	0.29
2.74	2.74	1.47	2.77	0.01	0.01	0.02	-	0.01	0.35
2.76	2.37	2.23	2.34	0.02	-	0.03	-	0.01	0.49
2.98	2.11	1.51	2.26	0.02	0.01	0.01	-	-	0.40
2.98	2.11	1.51	3.26	0.02	0.01	0.01	0.01	-	0.32
3.08	2.03	1.46	3.25	0.01	-	0.03	-	-	0.31
Average composition									
2.90	2.29	1.65	2.87	0.01	0.01	0.02	0.03	-	0.37
Standard deviation									
0.14	0.26	0.30	0.43	0.01	0.01	0.01	0.04	-	0.02

* as determined by electron-microprobe analyses; the data are recast on a $O_{10}(OH)_8$ basis. Fe is assumed to be divalent.

Single crystals of *amphibole* and amphibole relicts that were not replaced by the late magmatic quartz–K-feldspar assemblage were affected by partial to total replacement by (1) corrensite–dolomite, or (2) chlorite–corrensite–dolomite. The first was observed in the least altered samples of the granitic rock. The secondary minerals appear initially in cleavages and microcracks, outlined by small leucoxene grains, and subsequently in amphibole cores. In the assemblage chlorite–corrensite–dolomite, the chlorite appears along cleavages and microcracks of the amphibole (lenticular patches or spherulites). In some cases the primary mineral is reduced to isolated relicts. In the vicinity of the corrensite veinlets, large crystals of dolomite (50–100 µm) associated with corrensite and leucoxene replaced the amphibole relicts (Fig. 3).

Orthoclase and microcline are generally little affected by alteration processes except along the walls of chlorite or chlorite–corrensite veins; at these sites the feldspars have been invaded by the phyllosilicates. In addition, the replacement reaction plagioclase → albite + white mica + calcite has been extensive in the strongly chloritized parts of the samples.

CRYSTALLOCHEMICAL PROPERTIES OF SECONDARY MINERALS

The *chlorite* is of the IIb polytype. Two distinct homogeneous populations of chemical compositions are distinguishable (Table 3). Chlorite derived from biotite is characterized by low Si (2.88 ± 0.07) and by an Fe/(Fe + Mg) ratio of 0.35 (0.39 for parental biotite). That formed from amphibole has higher Si (3.02 ± 0.07) and an Fe/(Fe + Mg) ratio of 0.30 (0.28 for parental amphibole). These differences indicate the influence of local chemical controls due to the composition of the host mineral. Chlorite compositions are less homogeneous in veins or in veinlets: Si is more variable (2.90 ± 0.14) and the Fe/(Fe + Mg) ratio ranges from 0.30 to 0.50. In spite of this variability, the chlorite in veins is richer in iron than that formed at the expense of biotite and amphibole.

Corrensite in its air-dried state is characterized by a 28.3 Å reflection which shifts to 31 Å after glycol saturation. After heating to 550°C for 2 hours, the remaining (001) reflection occurs at 12.07 Å, showing that chlorite is regularly interstratified with saponite. This is consistent with a 50% chlorite – 50% smectite ordered type (Inoue 1985). Chemically, corrensite is distinguished readily from chlorite by its higher Si [3.30 average per $O_{10}(OH)_8$] and higher Na,Ca,K (Table 4). Aluminum content is lower, as is the Fe/(Fe+Mg) ratio (0.28 on average). In the diagram Al–Fe–Mg, corrensite compositions form a separate population that has about the same Al/Fe ratio as chlorite (Fig. 4).

White micas formed as alteration products in plagioclase are of the $2M_1$ polytype. They are phengitic, and substitution for octahedral Al is only 0.03 Fe and 0.06 Mg atoms (Table 5). Interlayer charge ranges from 0.90 to 0.95 per $O_{10}(OH)_2$. This charge is mainly satisfied by potassium ions: the Na/(Na+K) ratio is less than 0.01.

The *carbonates* were analyzed systematically in amphibole relicts (55 analyses) and in the different types of veins (50 analyses). Two groups of compositions exist: dolomite $Fe_{0.07\pm0.06}Mg_{0.83\pm0.06}$

TABLE 4. CHEMICAL COMPOSITION OF CORRENSITE*

Si	Al	Fe^{2+}	Mg	Ti	Mn	Ca	Na	K	$\frac{Fe}{Fe+Mg}$
In amphibole									
3.20	1.97	1.40	3.08	0.01	0.02	0.05	0.07	0.02	0.31
3.20	1.90	1.39	3.17	–	0.04	0.06	0.12	0.02	0.30
3.46	1.63	1.32	3.22	0.01	0.01	0.05	–	0.03	0.29
3.35	1.67	1.29	3.38	–	0.01	0.06	0.03	0.04	0.28
3.47	1.56	1.38	3.15	0.02	0.02	0.07	0.04	0.06	0.30
3.53	1.47	1.33	3.23	0.03	–	0.09	–	0.03	0.29
3.36	1.56	1.42	3.45	–	–	0.05	–	0.03	0.29
3.31	1.63	1.55	3.18	0.02	–	0.10	0.08	0.02	0.33
3.11	1.75	1.60	3.41	–	–	0.06	0.09	0.01	0.32
3.21	1.93	1.38	3.06	0.04	–	0.11	0.06	0.02	0.31
Average composition									
3.35	1.72	1.29	3.29	0.01	0.01	0.06	0.04	0.03	0.28
Standard deviation									
0.20	0.29	0.28	0.27	0.01	0.01	0.04	0.04	0.01	0.02
In fissures									
3.06	2.07	1.41	3.31	0.01	–	0.04	0.03	0.02	0.30
3.11	1.98	1.23	3.48	0.01	0.02	0.03	0.06	0.02	0.26
3.11	2.00	1.23	3.49	–	–	0.02	0.08	–	0.26
3.06	2.06	1.36	3.30	0.02	0.01	0.03	0.06	0.04	0.29
3.42	1.59	0.93	3.65	0.01	–	0.14	0.04	0.04	0.20
3.42	1.70	1.07	3.37	0.01	–	0.09	0.07	0.03	0.24
3.14	2.05	1.46	3.12	0.01	0.02	–	0.05	–	0.32
3.36	1.88	0.96	3.43	–	–	0.06	–	0.02	0.22
3.68	1.40	0.99	3.40	0.03	0.01	0.08	–	–	0.23
3.16	2.05	1.27	3.26	0.01	0.01	0.04	0.01	–	0.28
3.27	1.51	1.57	3.47	0.01	–	0.05	0.14	0.04	0.31
Average composition									
3.30	1.82	1.29	3.26	0.01	0.01	0.06	0.05	0.02	0.28
Standard deviation									
0.26	0.31	0.40	0.33	0.01	0.01	0.04	0.05	0.02	0.02

*as determined by electron-microprobe analyses; the data are recast on a $O_{10}(OH)_8$ basis. Fe is assumed to be divalent.

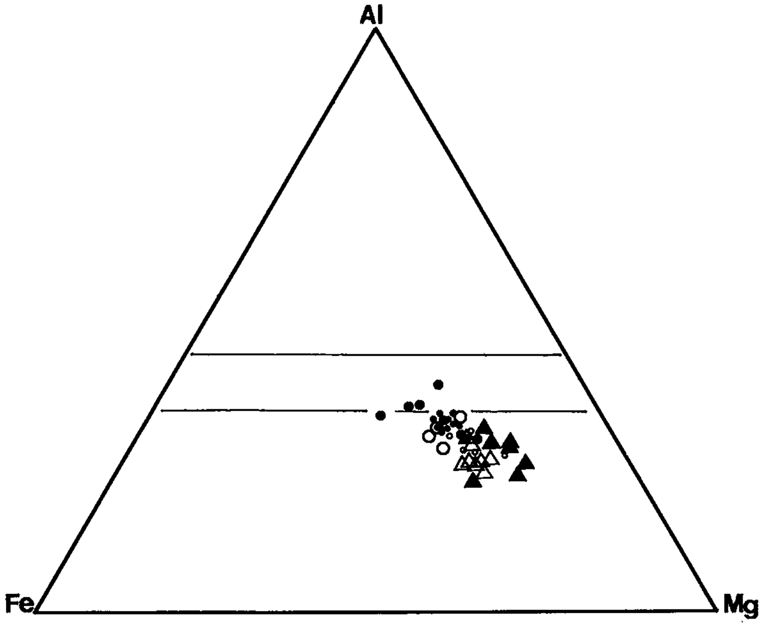

FIG. 4. Compositions of chlorite (circles) and corrensite (triangles) in the Al–Fe–Mg system. The composition field of metamorphic chlorite is given by the horizontal band (Velde & Rumble 1977). Symbols: filled circles: vermicular chlorite; small filled circles: chlorite replacement of biotite; open circles: chlorite growths on (001) biotite faces; small open circles: chlorite from amphibole; filled triangles: corrensite in veins; open triangles: corrensite from amphibole.

TABLE 5. CHEMICAL COMPOSITION OF WHITE MICA IN ALTERED PLAGIOCLASES*

Si	Al	Fe	Mg	Ti	Mn	Ca	Na	K
3.13	2.74	0.04	0.12	-	-	-	-	0.94
3.10	2.89	0.01	0.02	-	-	-	-	0.87
3.11	2.80	0.04	0.03	-	-	0.01	0.01	0.92
3.06	2.90	0.02	0.01	-	-	0.01	0.01	0.95
3.06	2.84	0.05	0.10	0.01	-	0.01	0.02	0.86
3.06	2.90	0.02	0.05	0.01	0.01	0.01	0.01	0.88

* as determined by electron microprobe analyses; the data are recast on a $O_{10}(OH)_2$ basis. Fe is assumed to be divalent.

$Ca_{1.02\pm0.06}(CO_3)_2$, and calcite $Fe_{0.01\pm0.01}Mg_{0.06\pm0.06}Ca_{1.98\pm0.06}(CO_3)_2$. The presence of these two types of carbonates was checked by X-ray diffraction.

DISCUSSION

The mineralogical composition of veins and altered zones of the rocks is complex: three phyllosilicate phases (chlorite, corrensite, phengite) are apparently asociated with two carbonate phases (calcite, dolomite) and two types of oxides (leucoxene, hematite). Have these minerals crystallized during a single hydrothermal event, therefore representing the evolution of physicochemical parameters with time, or have they crystallized during several superimposed hydrothermal events? The petrological relationships between carbonate phases in veins indicate that the dolomite plus hematite association was precipitated after the reopening of calcite veins. Corrensite is always either associated with dolomite in the wallrocks, or it crystallized near the dolomitic veins. On the other hand, dolomite vein fillings are not necessarily accompanied by corrensite. Where corrensite is absent, amphibole remains unaffected and shows, therefore, that alteration of wallrock is not regularly organized along the dolomite veins. The distribution of chlorite is different: this secondary phase appears progressively first by growths on (001) faces of biotite, and then by a more extensive replacement of the mica, thereby affecting large volumes of rock. The intensity of the chloritization process increases strongly in the vicinity of large calcitic veins, where wallrocks are corroded by vermicular chlorite.

In summary, the petrological observations indicate that the effects of two hydrothermal events are superimposed, as sketched in Figure 5. The first event is a pervasive propylitic alteration that has affected large volumes of rock (Lowell & Guilbert

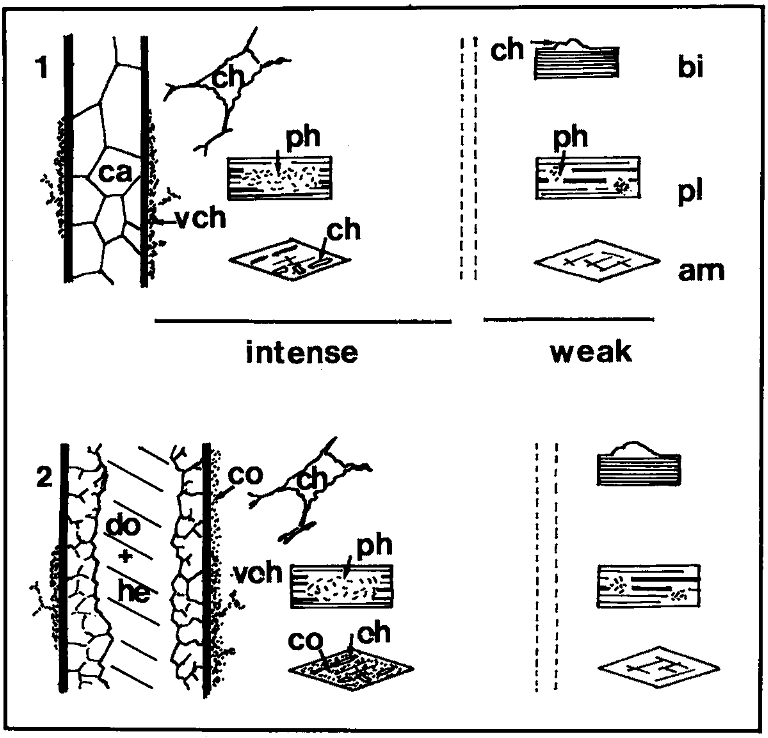

FIG. 5. Schematic representation of the relationships between the propylitic alteration type (1) and the corrensite–dolomite hematite event (2). bi: biotite; pl: plagioclase; am: amphibole; ca: calcite; vch: vermicular chlorite; ph: phengite; ch: chlorite; co: corrensite; do: dolomite; he: hematite.

1970). Chlorite crystallized at the sites of the primary ferromagnesian phases. The intensity of the reaction increased toward the large calcite veins; the maxium reaction was attained at the fracture walls, where all primary phases were replaced by the vermicular iron-rich chlorite. Chloritization of the biotite is more intense than that of amphibole. The second episode of alteration affected only the amphibole; the chlorite that had formed from amphibole and biotite, and the relicts of biotite, were not affected by the crystallization of corrensite. Amphibole grains near dolomite + hematite veins were replaced by corrensite + dolomite, especially in reopened large (200 μm) calcitic veins. The reopening of sealed fractures in hydrothermal or metamorphic environments is common (Ramsay 1980, Gratier 1984).

Processes of propylitic alteration

The chloritization process that affected the "Les Crêtes" granite produced petrological features similar to those of propylitic alteration in other granites (Parneix *et al.* 1985, Parneix & Meunier 1984). These effects include: 1) chlorite growths on (001) faces of biotite in contact with quartz, and progressive replacement of the mica by chlorite in areas where the reaction is more advanced; 2) total replacement of biotite, producing a secondary set of microfissures that are sealed by chlorite or calcite. In these very intensely altered facies, the walls of calcitic veins are corroded by vermicular iron-rich chlorite.

The chemical composition of the chlorite in classic examples of propylitic alteration is variable, and is dependent on the site of crystallization. The iron content is highest in the vermicular habits, as is typical (Lacroix 1896, Meunier & Proust 1982). The Fe/(Fe + Mg) ratios of primary minerals in which the chlorite crystallized are approximately conserved: amphibole 0.28 → chlorite 0.30, biotite 0.39 → chlorite 0.35. The effect of local equilibria is obviously expressed in the propylitic type of alteration.

As the chloritization reaction involved very small volumes of amphibole relative to volumes of biotite, the effect of chloritization of amphibole on the large-scale chemical balance may be neglected. Parneix *et al.* (1985) showed that the trend of hydrothermal chloritization in propylitic rocks is toward an exchange of 1 biotite → 1 chlorite, resulting in a 30% volume increase. The increase is accommodated by the growth of chlorite on (001) faces of biotite, and by chloritic sealing of secondary microcracks. The reaction cannot be considered to conserve aluminum, since this would induce a volume decrease of about 13% (Ferry 1979). Assuming that a similar volume increase was incurred in the "Les Crêtes" altered granite, the overall chemical balance in the propylitized zones can be explained by two types of ion transfers: 1) exchange of K^+ from chloritized biotite to the neighboring plagioclase, and exchange of Al^{3+} from plagioclase to biotite; Ca^{2+} ions are transferred to fracture solutions and eventually are consumed by calcite precipitation; 2) exchange between the flowing solutions and the rock by H_2O + CO_2 + Fe^{2+} + Mg enrichment of the solid phases and leaching of Na + Si^{4+}.

The contribution of fluids to the Fe–Mg enrichment of the altered rock has been demonstrated both in the chloritization reaction where Al is conserved (Ferry 1979), and in the reaction where volume is increased (Parneix *et al.* 1985). Fe–Mg enrichment in altered zones of the "Les Crêtes" granite is exemplified by the crystallization of iron-rich vermicular chlorite within the walls of the calcite veins. This also may explain the formation of phengitic mica in plagioclase whose alteration into clay + calcite controls $P(CO_2)$ (Giggenbach 1981).

Corrensite + dolomite + hematite alteration event

Corrensite appears only in amphibole. The extent of replacement increases toward the dolomite + hematite veins, except that some wallrock has not been affected, probably because of local impermeability.

As the amphibole is a Si- and Ca-rich variety, its destabilization creates microsystems where the chemical potentials of these elements are locally high. The theoretical demonstration of mosaic or local equilibria in rocks can be found in Korzhinskii (1959) and Thompson (1959). These local conditions promote the crystallization of corrensite instead of chlorite, but the conditions are probably not sufficiently aggressive to destabilize chlorite. This can explain why corrensite has approximately the same Fe/(Fe + Mg) ratio as chlorite where they coexist inside amphibole crystals; if these phases had crystallized simultaneously the chlorite component would have preferentially fixed iron ions, whereas corrensite would have fixed magnesium ions (Velde 1985).

Temperature conditions

Hydrothermal chlorite is stable between 130 to 300°C (Cathelineau & Neiva 1985). Corrensite has been reported to occur over a similar temperature range (150 to 280°C) in basalts and pyroclastics (Velde 1985), but the mineral also crystallizes as a step in the transformation of saponite into chlorite as temperature increases (Inoue *et al.* 1984, Inoue 1985). This reaction is common in diagenesis and in active geothermal fields.

Although the reopening of calcite veins in the "Les Crêtes" granite may have initiated a temperature decline, temperature does not seem to be a significant parameter in governing the crystallization of corrensite. This interpretation is based on the apparent absence of the sequence: saponite → corrensite → chlorite in the hydrothermal alteration of intrusive rocks.

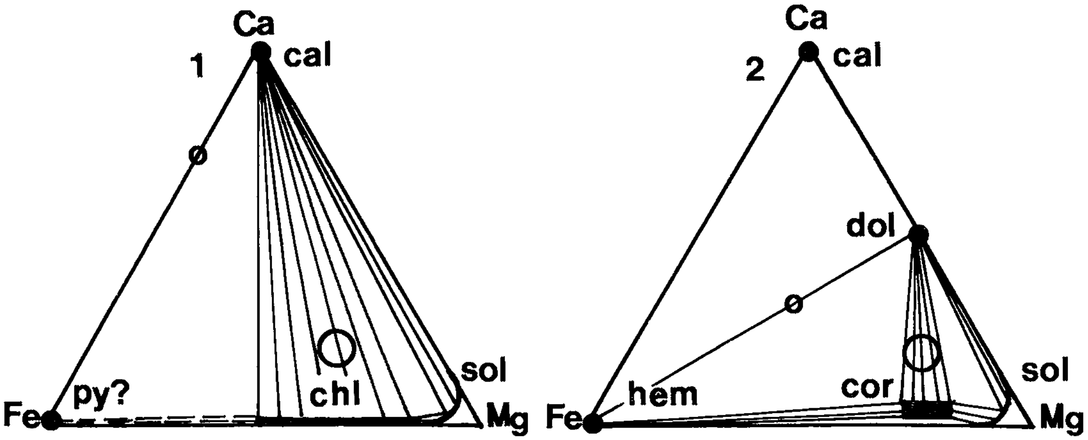

FIG. 6. Phase diagrams in the Ca–Fe–Mg system showing the relationships between phase precipitated in veins (small circles) and phases that replaced primary minerals in wallrocks (large circles) during the propylitic alteration (1) and the corrensite event (2). Symbols: cal: calcite; py: pyrite; chl: chlorite; sol: magnesian solution; hem: hematite; dol: dolomite; cor: corrensite.

Chemical conditions

Among the chemical conditions that controlled the secondary paragenesis in the two hydrothermal events, the composition of fluids obviously changed. Carbonates were precipitated in both alteration processes, and so the pH conditions were not substantially dissimilar. The main differences between the fluids were: 1) high Fe^{2+} chemical potential and low $f(O_2)$ (no Fe-oxide formation) for the propylitic fluid; 2) high Mg^{2+} chemical potential and high $f(O_2)$ (crystallization of hematite) in the later fluid. Because the Mg–Fe solid solution of chlorite is more extended than that of corrensite (Brigatti & Poppi 1984), Fe/Mg ratio of the fluids cannot be considered as the controlling factor for the crystallization of these minerals. That being the case, corrensite evidently is the stable phase in oxidative conditions, whereas chlorite is the stable phase in more reducing conditions. The tentative phase relations are shown in Figure 6.

CONCLUSION

Corrensite was classically considered to be a transitional step in the saponite ⇄ chlorite reaction (reaction toward the right in active geothermal fields or in diagenetic environments; reaction toward the left in weathering processes). Our study shows that corrensite behaves as an independent phase in hydrothermal alteration of granitic rocks, and that its crystallization in place of chlorite seems to depend more on redox conditions than on temperature. The minor effect of temperature is indicated by the fact that corrensite is known to crystallize in conditions that vary from hydrothermal to surface (room-temperature). In contrast, the importance of $f(O_2)$ is that it determines the oxidation state of iron, which is mostly ferric in corrensite (Brigatti & Poppi 1984) and ferrous in trioctahedral chlorite (Newman & Brown 1987).

If corrensite is a truly independent phase whose crystallization is governed by $f(O_2)$, then the reaction saponite → chlorite is not totally temperature-dependent. Two mineral reactions must be distinguished: 1) saponite → corrensite, 2) corrensite → chlorite. They proceed successively in diagenesis (1→2) and in weathering (2→1) because these two environments are characterized by a gradual change in redox conditions. This implies that a third reaction is theoretically possible if chemical conditions remain reducing when temperature varies: 3) saponite (stevensite)→chlorite.

ACKNOWLEDGEMENTS

The authors thank Dr. S.J. Guggenheim, D.R. Peveár, and an anonymous referee for their critical reading of the work. Thanks are also due to Dr. B. Velde for valuable discussion. This investigation was made possible through the financial support of the *Action Thématique Programmée "Transfert"* from the *Institut d'Astrophysique du Globe.*

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Received April 22, 1987; revised manuscript accepted October 7, 1987.