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GREENALITE, STILPNOMELANE, MINNESOTAITE, CROCIDOLITE AND CARBONATES IN A VERY LOW-GRADE METAMORPHIC PRECAMBRIAN IRON-FORMATION

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ABSTRACT

The Sokoman Formation in the Howells River area, at the western edge of the Labrador Trough, is part of a relatively undisturbed sedimentary sequence which dips between 5° and 12° east-northeast. The finely banded silicate-carbonate members of this iron-formation were studied by detailed petrographic and electron microprobe techniques. Most of the assemblages show complex textures in which early diagenetic features are overprinted by later ones which are the result of very low-grade metamorphic reactions. Of the three Fe-silicates, greenalite, stilpnomelane, and minnesotaite, greenalite appears to be of very early origin (sedimentary to diagenetic). Stilpnomelane appears to be of diagenetic origin, and minnesotaite probably began its formation in diagenetic stages as well, but is generally concluded to be of very low-grade metamorphic origin. Greenalite which occurs as oolites, granules, and later cement, is cryptocrystalline to microcrystalline in texture, and of homogeneous chemical composition. Stilpnomelane is well-crystallized, at times medium-grained. Minnesotaite, in well-crystallized rosettes and sprays, replaces earlier greenalite and stilpnomelane as well as much of the associated carbonates. Carbonate compositions are represented by members of the dolomite-ankerite series, siderite, and calcite. Ankerite and siderite are the most common carbonate species. Manganoan dolomite occurs in well-crystallized oolites which show relict banding as outlined by discontinuous concentric bands of siderite rhombohedra. Calcite occurs sporadically as cement around silicate granules and in granular occurrences of calcite-siderite pairs. Magnetite occurs in coarsely recrystallized bands, oolites, granules and irregular masses. Quartz or chert occur throughout all of the assemblages. Crocodolite is found only in highly deformed, crenulated crocodolite-magnetite-stilpnomelane-quartz assemblages in exposures near Schefferville, P.Q., and northwest thereof, where bulk compositions are Na-rich and structural deformation is pronounced. The primary Fe-silicate materials were probably hydrous silicate gels of greenalite-type and stilpnomelane-type compositions. Greenalite and stilpnomelane appear to be the recrystallization products thereof. Minnesotaite is a reaction product of earlier silicate and carbonate-chert assemblages. All carbonates and magnetite appear to be of primary origin but are now coarsely recrystallized. Although recrystallization and reaction textures are present in all assemblages, replacement textures indicative of possible solution of earlier phases and deposition of later phases were not found.

INTRODUCTION

The mineral assemblages in this study are part of the silicate-rich horizons of the Protero-

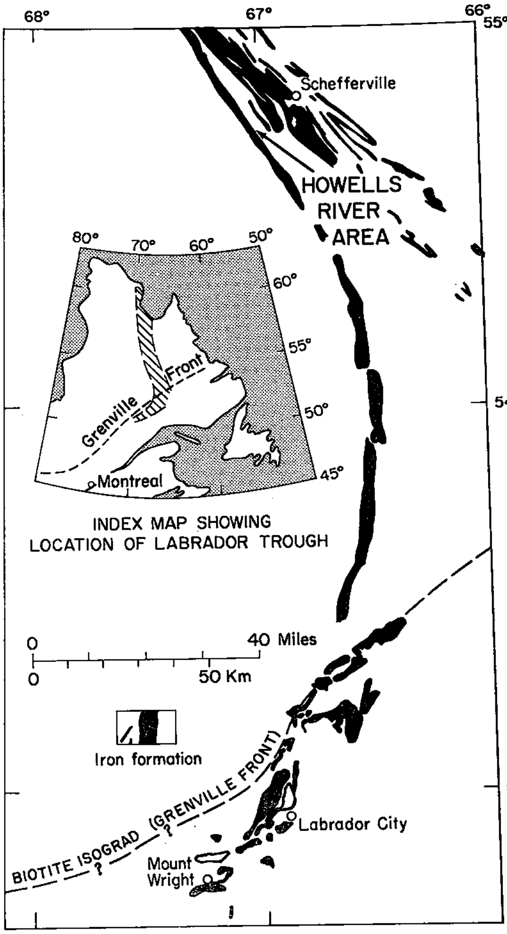

FIG. 1. Location of the Howells River area, Newfoundland and Schefferville, P.Q., with respect to the iron-formation horizons in the Labrador Trough (after Gross 1968). Location of biotite isograd after Fahrig (1967).

zoic iron-formation sequence at the western edge of the Labrador geosyncline. Most of the samples were obtained from the Sokoman Formation in the Howells River area which is located approximately twelve miles west of Schefferville, P.Q. (Fig. 1). Several additional samples were obtained from the Sokoman Formation in the iron mining district of Schefferville, P.Q., and 23 miles northwest thereof, in the Walthier Lake area.

The iron-formation sequence in the Howells River area was selected for this study of silicate-carbonate assemblages because the Sokoman Formation in this area is unleached, and because it probably is the least metamorphosed and least altered iron-formation in the Labrador Trough. Although the mineral assemblages display some very low-grade metamorphic features, all preserve diagenetic and possibly primary textures and chemistry.

GEOLOGIC SETTING IN THE HOWELLS RIVER AREA

The lowermost member of the Proterozoic Kaniapiskau Supergroup which unconformably overlies the Ashuanipi Basement complex of Archean age, is the Wishart Formation, a basal quartzite with an average thickness of approximately 58 feet (Fink 1972) in the Howells River area. This is overlain by the Ruth Slate, a thinly laminated slate consisting of carbonate, chert and greenalite and sporadic pyrite and graphite. The Ruth Slate averages 17 feet in thickness. The Sokoman Formation, with an average thickness of 373 feet, overlies the Ruth Slate. The most silicate-rich members of the Sokoman Formation in the Howells River area are referred to as the "Lower Iron Formation" (LIF) and the "Lean Chert" (LC) by Iron Ore Company of Canada geologists (Fink 1972). The Lower Iron Formation member directly overlies the Ruth Slate, whereas the Lean Chert member forms the uppermost member of the iron-formation sequence. The Lower Iron Formation member averages 27 feet in thickness and the Lean Chert member averages 83 feet in thickness. The majority of the assemblages of this study were obtained from the "LIF" and "LC" members of the Sokoman Formation in the Howells River region. Samples were obtained from diamond drill cores 1032D and 1039D of the Iron Ore Company of Canada (Fink 1971, 1972) and from field occurrences. A few additional samples of silicate-rich members of the Sokoman Formation, the silicate-carbonate iron-formation (SCIF) member and the "lower red cherty" (LRC) members were obtained in the Schefferville mining areas. One sample of Ruth Slate from the Schefferville mining area and one crocidolite-rich assemblage from Walthier Lake, 23 miles northwest of Schefferville, were also studied.

The Sokoman Formation in the Howells River area consists of conformable sedimentary units which are relatively undisturbed and strike approximately 35°NW and dip about 5 to 12° east-northeast. Faults and other evidence of structural deformation are extremely rare. The Sokoman Formation in the Schefferville area, however, has undergone complex structural changes and locally strong leaching and supergene enrichment.

The first detailed study of the geologic setting, mineralogy and petrology of the Sokoman Formation in the Howells River area was made by Perrault (1955).

ANALYTICAL METHODS

Detailed petrographic studies of mineral assemblages and their textural relations were made prior to electron probe microanalysis. Specific assemblages were photographed at a magnification similar to that of the highest power of the light optical system of the electron probe (640X). Chemical analyses for nine oxide components in the silicates, carbonates and oxides were performed on polished thin sections using a three-spectrometer Etec Autoprobe. Operating conditions were 15kv accelerating voltage and 0.02 microampere sample current, standardized on quartz, using beam current integration. The electron beam size was adjusted to a relatively large size of about 2 to 8 microns in diameter because of the possibility of breakdown of the hydrous silicates and the carbonates with a higher electron loading per unit area. A combination of well-analyzed, homogeneous synthetic silicate glasses and naturally occurring crystalline silicates was used as standard materials. The Etec Autoprobe spectrometers are controlled by an on-line PDP-11/05 (12*K* memory) computer which also performs the data handling for each analysis point. The computer program for partial instrument control and data handling was developed by Dr. Larry W. Finger of the Geophysical Laboratory, Washington, D.C. (Finger & Hadidiacos 1972; Finger 1973). Data reduction procedures were those of Bence & Albee (1965) with correction factors from Albee & Ray (1970).

Complete chemical analyses of bulk samples of the silicate-rich iron-formation were made by a combination of gravimetric, flame photometric and colorimetric techniques.

BULK CHEMISTRY OF SILICATE-RICH IRON-FORMATION

Complete chemical analyses of eight bulk samples of silicate-rich members of the Sokoman Formation and Ruth Slate are given in Table 1. Analyses 1 to 5 represent samples from the unleached and unaltered iron-formation in the Howells River area. In each of these, FeO exceeds Fe_2O_3, reflecting the presence of abundant siderite and Fe-silicates (which contain large amounts of FeO), and lesser amounts of magnetite. Oxide percentages in these five analyses are similar to those given by James (1966) for the silicate-carbonate iron-formation samples from the Mesabi district, Minnesota and the Gogebic district, Michigan. Analysis 6, from the Walthier Lake area, represents a structurally deformed and sheared assemblage of riebeckite, stillpnomelane, magnetite and quartz; Fe_2O_3 and Na_2O contents are much higher than in analyses 1 to 5. Analysis 7, which was made on a minnesotaite-rich band of the silicate-carbonate iron-formation member (SCIF) in the Schefferville mining area, is almost equivalent to that of pure minnesotaite (see Table 4 for comparison). Analysis 8, made on a highly oxidized part of the Ruth Slate, consists of hematite-limonite-chert and lesser, brown oxidized minnesotaite.

TABLE 1. CHEMICAL ANALYSES OF BULK SAMPLES OF SILICATE-RICH SOKOMAN FORMATION

	1	2	3	4	5	6	7	8
SiO_2	33.5	22.7	24.0	43.5	26.1	39.9	54.33	44.31
TiO_2	0.066	0.075	0.041	0.11	0.20	0.083	trace	trace
Al_2O_3	0.77	0.60	0.23	0.66	1.56	0.74	0.88	0.08
Fe_2O_3	11.7	8.94	23.2	n.d.*	7.23	32.1	2.57	48.75
FeO	29.6	32.3	40.5	32.6	36.8	16.1	32.06	0.28
MnO	0.86	1.78	0.64	1.53	0.94	0.15	0.52	0.02
MgO	3.42	4.54	1.32	4.33	4.54	4.56	4.22	0.03
CaO	1.98	9.21	0.90	5.46	0.69	n.d.	0.06	0.05
Na_2O	0.030	0.056	0.023	0.023	0.093	2.95	0.04	0.03
K_2O	0.31	0.31	0.17	0.17	0.36	0.12	0.05	0.03
$H_2O(+)$	1.17	2.97	3.19	4.38	1.19	2.45	5.08	6.03
$H_2O(-)$	0.17	0.38	0.13	0.07	0.51	0.27	0.02	0.05
P_2O_5	0.050	0.056	0.084	0.006	0.12	0.055	trace	0.04
CO_2	16.4	16.6	5.4	7.2	19.8	0.03	0.02	0.05
S	n.d.	n.d.	n.d.	0.005	0.030	0.010	0.041	0.074
C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	<0.02
Total	100.03	100.52	99.83	100.04	100.16	99.52	99.98	99.84

*n.d. - none detected. Analyses 1 to 6 by Maynard E. Coller, Dept. of Geology, Indiana University, Bloomington, Indiana. Analyses 7 and 8 by Hiroshi Haramura, Tokyo Institute of Technology, Tokyo.

1. Howells River area, D.D.H. 1032D at 183', from the Lower iron-formation member (LIF) consisting of magnetite, greenalite, stilpnomelane, chert, minnesotaite, ankerite and siderite.
2. Howells River area, D.D.H. 1039D at 130', from the Lean Chert member (LC), consisting of greenalite, stilpnomelane, minnesotaite, ankerite, magnetite, siderite, and trace of chert.
3. Howells River area, D.D.H. 1039D at 154', from the Lean Chert member (LC), consisting of greenalite, magnetite, minnesotaite, calcite, siderite and quartz.
4. Howells River area, D.D.H. 1039D at 186', from the Lean Chert member (LC), consisting of minnesotaite, greenalite, dolomite, siderite, stilpnomelane, magnetite, quartz, and minor calcite.
5. Howells River area, D.D.H. 1039D at 459', from the Lower iron-formation member (LIF) consisting of magnetite, stilpnomelane, minnesotaite, siderite and quartz.
6. Walthier Lake area, 23 miles northwest of Schefferville, Quebec, from bands of silicate-carbonate-iron-formation (SCIF) consisting of magnetite, crocidolite (riebeckite), stilpnomelane and quartz.
7. Schefferville mining area, silicate-carbonate iron-formation member (SCIF), consisting of minnesotaite (95-98%), and traces of quartz and magnetite.
8. Schefferville mining area, Ruth Slate, consisting of chert, hematite, limonite, and brown, oxidized minnesotaite.

MINERAL CHEMISTRY

Many of the minerals in this only very slightly metamorphosed iron-formation are very fine-grained and finely intergrown with each other. Although such assemblages are difficult to study by methods which require mineral separation and concentration, a combination of detailed petrography and quantitative electron probe microanalysis allows for chemical and textural characterization of all of the coexisting phases.

The minerals which make up this silicate-rich iron-formation are, in approximate decreasing order of abundance: greenalite, stilpnomelane, minnesotaite, magnetite, chert (or quartz), carbonates (members of the dolomite-ankerite series, siderite and calcite) and locally small amounts of crocidolite (riebeckite). The chemistry of these are treated in the above order in the subsequent section.

Greenalite

Greenalite, which may be chemically characterized as $(Fe,Mg)_6Si_4O_{10}(OH)_8$, is structurally the Fe-rich analogue of antigorite (Gruner 1936). Published wet chemical analyses (*e.g.* Leith 1903; Gruner 1936, 1946; and other references in Table 2) show large amounts of Fe_2O_3, ranging from 8.40 to a maximum of 34.85 wt. % as reported in an analysis given by Gruner (1936). Whether all or some of this ferric iron component is part of the original structure or whether it results from oxidation during burial, or subsequent weathering, is still unknown. Al_2O_3 ranges only from trace amounts to a maximum of 3.03 wt. % (Cochrane & Edwards 1960). Except for a considerable range in MgO, other oxide components are generally present in amounts less than 1 wt. %, although analysis no. 3 (Table 2) gives an Na_2O content of 1.4 weight per cent. The high Na_2O (1.4 wt. %) in analysis 3 of Table 2 might be due to a 5 to 6 % admixture of an unidentified mineral (Zajac 1972).

The complete analyses in Table 2 have been recalculated on the basis of 18(O,OH) per formula unit and on an anhydrous basis, for ease of comparison with the electron probe data. The microprobe analyses have been recalculated on an anhydrous basis of 14 oxygens in which the

TABLE 2. REPRESENTATIVE COMPLETE ANALYSES AND ELECTRON MICROPROBE ANALYSES OF GREENALITE

	1	2	3	4	5	6	7	8
SiO_2	32.02	32.27	35.87	36.0	32.91	32.73	32.89	32.29
TiO_2	---	0.05	0.25	n.d.	0.07	0.00	0.02	0.09
Al_2O_3	1.01	3.03	0.51	0.1	1.90	1.52	1.52	1.61
Fe_2O_3	22.95	14.83	14.55	48.5†	50.32†	51.27†	52.51†	50.90†
FeO	29.15	36.00	35.18					
MnO	---	0.87	1.76	0.1	0.20	0.34	0.43	0.59
MgO	5.34	2.11	3.65	4.4	3.11	1.29	1.43	2.36
CaO	---	trace	0.03	trace	0.00	0.03	0.07	0.17
Na_2O	---	0.14	1.4	n.d.	0.15	0.06	0.00	0.08
K_2O	---	0.10	0.00	0.0	0.05	0.00	0.00	0.01
$H_2O(+)$	9.52	8.71	6.66	10.9††	11.29††	12.76††	11.13††	11.90††
$H_2O(-)$	---	2.37	0.04					
Total	99.99	100.48	99.90**	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)

Recalculated on basis of

	1				2				3				4		5		6		7		8	
	18(O,OH)		14 Oxygens		18(O,OH)		14 Oxygens		18(O,OH)		14 Oxygens		← 14 Oxygens →									
Si	3.699	3.84	3.883	4.00	3.874	4.00	3.917	4.00	4.322	4.32	4.126	4.13	4.222	4.22	3.960	4.00	4.043	4.04	4.004	4.00	3.950	4.00
Al	0.137		0.117		0.126		0.083		0.000		0.000		0.000		0.040		0.000		0.000		0.050	
Al	0.000	5.73	0.027	6.04	0.302	5.77	0.351	5.89	0.072	6.12	0.069	5.95	0.014	5.55	0.230	5.92	0.221	5.81	0.219	5.88	0.182	5.93
Ti	0.000		0.000		0.004		0.005		0.022		0.022		0.000		0.006		0.000		0.002		0.009	
Fe^{3+}	1.995		5.053†		1.340		5.011†		1.319		4.644†		4.757†		5.062†		5.296†		5.346†		5.208†	
Fe^{2+}	2.816				3.614				3.545													
Mn^{2+}	0.000		0.000		0.088		0.089		0.180		0.172		0.010		0.021		0.036		0.044		0.061	
Mg	0.919		0.965		0.377		0.382		0.655		0.626		0.769		0.558		0.237		0.260		0.431	
Ca	0.000		0.000		0.000		0.000		0.004		0.004		0.000		0.000		0.004		0.009		0.022	
Na	0.000		0.000		0.032		0.033		0.327		0.312		0.000		0.034		0.014		0.000		0.011	
K	0.000		0.000		0.016		0.015		0.000		0.000		0.000		0.007		0.000		0.000		0.002	
OH	7.336				6.975				5.354													

---not determined; n.d.* none detected ** 0.06 wt. % F also present, making analysis total 99.96 † total Fe recalculated as FeO only
†† H_2O values obtained by subtracting electron microprobe total from 100%

1. Biwabik Iron Formation, Minnesota (Gruner 1946). 2. Greenalite granules, Roper River Iron Formation, Australia (Cochrane & Edwards 1960). 3. Greenalite of medium grain size, Sokoman Formation, Canada (Zajac 1972). 4. Greenalite granule, Gunflint Iron Formation, Ontario, Canada (Floran & Papike 1973). 5. D.D.H. 1032D, depth 183'; greenalite granules in chert, with ankerite (anal. 5, Table 5), brown stilpnomelane, magnetite, minnesotaite, and minor siderite (anal. 1, Table 6). 6. D.D.H. 1039D, depth 154'; greenalite cement around composite granules of magnetite, greenalite and minnesotaite. Other cements next to greenalite are calcite (anal. 1, Table 7) and chert. 7. D.D.H. 1039D, depth 154'; greenalite granule with siderite edge (anal. 5, Table 6) embedded in coarse-grained manganoan siderite matrix ($Fe_{1.27}Mg_{0.19}Mn_{0.48}Ca_{0.06}$). 8. D.D.H. 1039D, depth 166'; small greenalite granule enclosed in larger carbonate granule which consists mainly of manganoan dolomite with composition ($Ca_{1.00}Fe_{0.19}Mg_{0.47}Mn_{0.34}$).

8(OH) groups in the formulation of $Fe_6Si_4O_{10}(OH)_8$ are considered equivalent to 4 oxygens. As no information can be obtained in electron probe techniques on the oxidation state of the elements, all iron has been recalculated as FeO. Some of the analyses in Table 2 (nos. 3 and 4) show atomic Si contents which are considerably larger than 4.00. During electron probe analysis of greenalite granules it is not uncommon to obtain SiO_2 contents that exceed stoichiometric requirements. Floran (personal communication) finds similar high Si values in analyses of greenalite from the Gunflint Iron Formation. As the mineral is commonly extremely finely intergrown with chert, it seems probable that the erroneously high Si values are caused by submicroscopic intergrowths with chert. Although the analyses in Table 2 were made on greenalites from highly variable assemblages their compositional range is remarkably small. Electron probe analyses were made on green greenalite granules, on surrounding light green greenalite cement as well as dark brownish-green greenalite oolites and granules, but no distinctive changes in composition were found. It is concluded that the changes in colour and intensity of coloration are due to changes in the Fe^{3+}/Fe^{2+} ratio.

In thin section the colour of greenalite varies from olive green to dark greenish brown. Because of its generally extremely fine grain size, it may appear isotropic under doubly polarized light (Gruner 1946). All greenalites of this study occur in felted masses and show a grain size of about one micron or less for individual crystallites; they exhibit bluish-grey interference colours. Zajac (1972) reports one occurrence of tabular greenalite porphyroblasts (200 to 800 microns long) in a finer-grained greenalite matrix. This coarse greenalite, which is pleochroic from pale yellow to green, was used for analysis 3 in Table 2. This greenalite occurs in the Sokoman Formation adjacent to a diabase dyke. Zajac (1972) interprets the increase in grain size to be due to contact metamorphic effects. This occurrence is exceptional because almost all known greenalites are extremely fine-grained even though the associated minerals show well-developed medium- to coarse-grained recrystallization textures. This general tendency of greenalite not to recrystallize to a coarser grain size may be due to possible stacking mismatches and misfits between the atomic layers in the structure. In the Mg-analogue of greenalite, antigorite, these layers are undulating and may show considerable misfit (Kunze 1956).

Stilpnomelane

The earliest and most complete chemical, physical and structural data on stilpnomelane were obtained by Gruner (1937) on material from the Mesabi Range and by Hutton (1938) on stilpnomelane from metamorphic assemblages in Otago, New Zealand. The chemistry of stilpnomelane is considerably more complex than that of the other two associated Fe-silicates, greenalite and minnesotaite.

The crystal structure of stilpnomelane has been determined recently by Eggleton (1972) who suggests the following average formula:

$$(Ca,Na,K)_4\ (Ti_{0.1}Al_{2.3}Fe_{35.5}Mn_{0.8}Mg_{9.3})\ (Si_{63}Al_9)\ (O,OH)_{216}\cdot nH_2O$$

If stilpnomelane is considered to be mainly a hydrous Fe-Mg-Al silicate, this formulation can be simplified to $(Fe,Mg,Al)_{2.7}(Si,Al)_4\ (O,OH)_{12}\cdot xH_2O$. This formulation facilitates comparison with the chemistry of greenalite, $Fe_6Si_4O_{10}(OH)_8$ and minnesotaite, $Fe_3Si_4O_{10}(OH)_2$. The structure of stilpnomelane has features which are present in talc (or minnesotaite), in trioctahedral micas, and in antigorite (or greenalite), as well as large cavities for Na, K, Ca, and H_2O as in zeolitic structures (Eggleton 1972).

A large variation in Fe_2O_3 content is reflected in published analyses (Table 3) with a range from a low of 2.90 wt. % (Trendall & Blockley 1970) to a high of 33.24 wt. % Fe_2O_3 (Ayres 1940). How much of this ferric component is part of the original, unaltered and unoxidized stilpnomelane structure is uncertain. Robinson (1969) has shown that green ferro-stilpnomelane in metamorphic assemblages from Otago, New Zealand, may weather to brown ferri-stilpnomelane on the outer surface. Zen (1960) has suggested that most primary stilpnomelane is ferrous in composition. In one of the occurrences in this study (D.D.H. 1039, depth 459′) light green stilpnomelane in chert-rich bands with minor magnetite alternates with dark brown stilpnomelane in siderite-magnetite bands. As the mineralogically distinct bands are finely interlayered, and as outcrop weathering is not a factor in this occurrence, it seems probable that the two types of stilpnomelane have dissimilar Fe^{3+}/Fe^{2+} ratios as a result of variations in the original, sedimentary or diagenetic conditions. Analysis 10 (Table 3) was made on a green stilpnomelane; an analysis of the adjoining brown stilpnomelane showed no distinctive chemical differences.

H_2O in published analyses of stilpnomelane shows a large range of values. Eggleton's (1972) recalculation of 48 complete analyses on the basis of (Si+Al+Ti+Fe+Mn+Mg) = 120 results in OH values ranging from 10.7 to 48.7. H_2O values in the same analyses range from 0.2 to 72.0. The average (OH) in Eggleton's table 4a for 37 representative analyses is 28.7,

TABLE 3. REPRESENTATIVE COMPLETE ANALYSES AND ELECTRON MICROPROBE ANALYSES OF STILPNOMELANE

	1	2	3	4	5	6	7	8	9	10
SiO_2	45.54	42.42	45.24	44.2	50.00	45.70	45.38	47.05	46.85	45.99
TiO_2	0.26	n.d.*	0.33	n.d.	0.00	0.07	0.00	0.08	0.00	0.04
Al_2O_3	4.75	6.71	6.73	4.5	4.25	5.30	4.48	4.22	4.20	4.23
Fe_2O_3	2.90	33.24	25.34	35.2†	26.20†	27.28†	33.50†	36.28†	36.70†	33.30†
FeO	25.38	0.85	3.45							
MnO	0.13	2.27	0.60	0.1	0.15	5.23	0.10	0.23	0.22	0.08
MgO	7.75	5.20	7.67	3.0	9.03	4.40	3.86	2.60	2.62	4.16
CaO	0.04	n.d.	1.91	0.4	0.20	0.35	0.53	0.21	0.05	0.35
Na_2O	0.82	trace	0.03	n.d.	0.08	0.02	0.15	0.42	0.42	0.28
K_2O	1.96	n.d.	1.67	2.0	0.07	0.69	1.47	1.25	1.06	2.16
$H_2O(+)$	8.46	8.33	6.72	10.6††	10.02††	10.96††	10.53††	7.66††	7.88††	9.41††
$H_2O(-)$	1.56	1.45	0.76							
Total	99.55**	100.47	100.45	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)

Recalculated on the anhydrous basis of 11 oxygens (total Fe as Fe^{2+} only)

	1		2		3		4		5		6		7		8		9		10	
Si	3.656	4.00	3.532	4.00	3.556	4.00	3.682	4.00	3.837	4.00	3.710	4.00	3.720	4.00	3.763	4.00	3.760	4.00	3.729	4.00
Al	0.344		0.468		0.444		0.318		0.163		0.290		0.280		0.237		0.240		0.271	
Al	0.105	3.27	0.190	3.14	0.180	3.20	0.124	3.20	0.221	2.98	0.217	3.07	0.153	3.15	0.161	3.13	0.157	3.13	0.133	3.20
Ti	0.016		0.000		0.020		0.000		0.000		0.004		0.000		0.005		0.000		0.002	
Fe^{2+}	1.879		2.144		1.727		2.452		1.681		1.852		2.297		2.427		2.464		2.258	
Mn^{2+}	0.009		0.160		0.040		0.007		0.010		0.360		0.007		0.016		0.015		0.005	
Mg	0.927		0.645		0.899		0.372		1.033		0.532		0.472		0.310		0.313		0.503	
Ca	0.003		0.000		0.161		0.036		0.016		0.030		0.047		0.018		0.004		0.030	
Na	0.128		0.000		0.005		0.000		0.012		0.003		0.024		0.065		0.065		0.044	
K	0.201		0.000		0.167		0.213		0.007		0.071		0.154		0.128		0.109		0.223	

n.d.* none detected; **additional elements listed: P_2O_5 0.44 and CO_2 0.28 wt. %, making analysis total 100.27 wt. %. †total Fe recalc. as FeO only
††H_2O obtained by subtracting electron microprobe total from 100%.

1. Ferrostilpnomelane from the Brockman Iron Formation, Hamersley Group, Australia (Trendall & Blockley 1970). 2. Stilpnomelane from iron-formation near Crystal Falls, Michigan (Ayres 1940). 3. Stilpnomelane from albite-stilpnomelane-actinolite schist, Otago, New Zealand (Hutton 1940).
4. Stilpnomelane granule from Gunflint Iron Formation, Ontario (Floran & Papike 1973). 5. Walthier Lake area, 23 miles northwest of Schefferville, Quebec; stilpnomelane-riebeckite (crocidolite)-magnetite-quartz assemblage (see Table 8, no. 5 for riebeckite analysis). 6. Franciscan Formation in Laytonville Quarry, Mendecino County, California; crossite (or ferroglaucophane depending on Fe^{2+}/Fe^{3+})-stilpnomelane-quartz schist (metachert of Chesterman 1966). A bulk analysis of this schist is as follows: SiO_2-82.4, TiO_2-0.15, Al_2O_3-4.40, Fe_2O_3-1.85, FeO-3.08, MnO-0.34, MgO-1.60, CaO 1.35, Na_2O-0.75, K_2O-0.82, $H_2O(+)$ 1.03, $H_2O(-)$ 0.04, P_2O_5-0.079, CO_2-0.37, S-0.040, total 98.30 wt. %. Spectrographically estimated Ni-0.05, Co 0.3 and Cu-0.3 wt. %. M.E. Coller, Indiana University, analyst (see Table 8, no. 6, for crossite analysis).
7. D.D.H. 1032D, depth 183'; brown, well-crystallized stilpnomelane in chert-ankerite-siderite bands (see Table 5, no. 5 for ankerite and Table 6, no. 1 for siderite analysis). 8. D.D.H. 1039D, depth 130'; brown, well-crystallized stilpnomelane adjacent to very fine-grained greenalite, euhedral magnetite and ankerite. 9. D.D.H. 1039D, depth 186'; brown, well-crystallized stilpnomelane in minnesotaite, greenalite, dolomite, siderite, magnetite and quartz assemblage. 10. D.D.H. 1039D, depth 459'; well-crystallized green stilpnomelane, pleochroic from almost colorless to medium green. Adjacent to brown stilpnomelane, quartz, magnetite, minnesotaite and siderite. The analysis of brown stilpnomelane is almost identical to the above, the colour variation being mainly a reflection of variable ferrous-ferric ratio.

out of a total of 216 (O,OH). In the above-mentioned, simplified formulation which was obtained by dividing by 18, the 216 (O,OH) reduce to 12 (O,OH) of which approximately 1 to 1.5 OH are part of the total 12 (O,OH). All analyses in Table 3 have been recalculated on the approximate and anyhdrous basis of 11 oxygens. The additional oxygens contributed by H_2O molecules in Eggleton's formulation were ignored because of the difficulty in distinguishing between absorbed and structural water by chemical analytical methods.

Al_2O_3 is clearly a major constituent in stilpnomelane, as can be seen from the selected analyses in Table 3. MgO is highly variable, with the most Mg-rich stilpnomelane in this study being from a stilpnomelane-crocidolite-magnetite-chert assemblage (analysis 5) and the least Mg-rich varieties being from greenalite-stilpnomelane-minnesotaite-carbonate-magnetite assemblages (analyses 8 and 9). MnO contents range from very small to several per cent. The highest MnO value (5.23 wt. %) in this study is found in analysis 6 for a stilpnomelane from the Franciscan Formation. K_2O as well as Na_2O are relatively major constituents in most analyses. Analysis 10 (Table 3) shows a K content of 0.223 per 11 oxygens. Na_2O is generally present in smaller amounts than K_2O. It is of interest to note that analyses 5 and 6 show very low Na_2O contents. In these relatively Na_2O-rich rocks the Na_2O component is concentrated in the coexisting Na-amphibole.

Most of the stilpnomelane occurrences in the Sokoman Formation of the Howells River area are pleochroic from light golden yellow to dark brown, suggesting a considerable ferric iron content. Some assemblages contain a colourless to light green pleochroic variety of stilpnomelane as well, and in one occurrence (Fig. 6C) brown and green stilpnomelane grains adjoin each other, reflecting variations in the oxidation state of the primary (depositional or diagenetic) assemblages. The texture of stilpnomelane is strikingly different from that of greenalite. Stilpnomelane occurs in well-recrystallized sheaves, sprays and bundles which frequently cross-cut very fine-grained greenalite granules and bands (Fig. 6D). In carbonate-chert-magnetite-stilpnomelane assemblages, the stilpnomelane sheaves are an integral part of the mosaic textures formed by recrystallization (Fig. 6B).

Minnesotaite

As shown by Gruner (1944), minnesotaite has a structure similar to that of talc $Mg_3Si_4O_{10}(OH)_2$.

TABLE 4. REPRESENTATIVE COMPLETE ANALYSES AND ELECTRON MICROPROBE ANALYSES OF MINNESOTAITE

	1	2	3	4	5	6	7
SiO_2	51.29	56.73	55.1	51.38	50.36	51.78	49.40
TiO_2	0.04	---	n.d.*	0.00	0.04	0.00	0.00
Al_2O_3	0.61	n.d.*	0.00	0.89	0.57	0.68	0.54
Fe_2O_3	2.00	2.39	23.4†	40.82†	42.62†	39.72†	39.45†
FeO	33.66	20.06					
MnO	0.12	---	trace	0.18	0.25	0.37	0.40
MgO	6.26	16.81	15.8	2.80	2.07	3.03	3.07
CaO	0.00	0.03	0.0	0.01	0.02	0.01	0.20
Na_2O	0.08	n.d.*	n.d.*	0.00	0.00	0.06	0.09
K_2O	0.03	n.d.*	0.0	0.49	0.35	0.31	0.25
$H_2O(+)$	5.54	3.83	5.7††	3.43††	3.72††	4.04††	6.60††
$H_2O(-)$	0.24	0.06					
Total	99.87	99.91	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)

Recalculated on the basis of

	1: 12(O,OH)		1: 11 oxygens		2: 12(O,OH)		2: 11 oxygens		3: 11 oxygens		4: 11 oxygens		5: 11 oxygens		6: 11 oxygens		7: 11 oxygens	
Si	3.801	3.86	3.948	4.00	3.986	3.99	3.971	3.97	3.953	3.95	3.949	4.00	3.930	3.98	3.981	4.00	3.934	3.99
Al	0.053		0.052		0.000		0.000		0.000		0.051		0.052		0.019		0.051	
Al	0.000	2.92	0.003	3.03	0.000	3.07	0.000	3.06	0.000	3.09	0.030	3.04	0.000	3.08	0.043	3.01	0.000	3.08
Ti	0.002		0.002		0.000		0.000		0.000		0.000		0.002		0.000		0.000	
Fe^{3+}	0.107		2.283†		0.127		1.301†		1.404†		2.624†		2.781†		2.554†		2.628†	
Fe^{2+}	2.085				1.178													
Mn^{2+}	0.009		0.008		0.000		0.000		0.000		0.012		0.017		0.024		0.027	
Mg	0.691		0.718		1.761		1.754		1.689		0.321		0.241		0.347		0.364	
Ca	0.000		0.000		0.002		0.002		0.000		0.001		0.002		0.001		0.017	
Na	0.012		0.012		0.000		0.000		0.000		0.001		0.000		0.009		0.014	
K	0.003		0.003		0.000		0.000		0.000		0.048		C.035		0.030		0.025	
OH	2.736				1.790													

--- not determined n.d.* none detected †total Fe recalculated as FeO only ††H_2O by subtraction of microprobe total from 100%

1. Biwabik Iron Formation, Minnesota (Gruner 1944). 2. Brockman Iron Formation, Hamersley Group, Australia (Trendall & Blockley 1970).
3. Gunflint Iron Formation, Ontario (Floran & Papike 1973). 4. D.D.H. 1039D, depth 130'; minnesotaite sprays formed from very fine-grained greenalite. 5. D.D.H. 1039D, depth 154'; minnesotaite sprays cutting across coarse-grained siderite ($Fe_{1.73}Mg_{0.14}Mn_{0.09}Ca_{0.04}$).
6. D.D.H. 1039D, depth 186'; minnesotaite rosettes formed inside greenalite bands and granules. 7. D.D.H. 1039D, depth 186'; minnesotaite sheaves cutting across edge of carbonate oolite consisting of dolomite ($Ca_{1.02}Mg_{0.58}Fe_{0.29}Mn_{0.11}$) and siderite ($Fe_{1.22}Mg_{0.23}Mn_{0.45}Ca_{0.10}$).

Chemical analyses of minnesotaite show that the only major substitution occurs between Mg and Fe, with almost all of the iron present as Fe^{2+} (Table 4, nos. 1 and 2). Other oxide components are generally considerably less than 1 wt. % each. Minnesotaite is chemically the simplest and the least hydrous of the three iron-silicates found in very low-grade metamorphic iron-formations. The complete analyses in Table 4 have been recalculated on the basis of 12(O,OH) as well as 11 oxygens, and the electron probe analyses have been recalculated on the same anhydrous basis of 11 oxygens. As the Fe^{3+} component is small, the two methods give essentially identical results. Minnesotaite analyses 1 to 3 (Table 4) are considerably more Mg-rich than those obtained in this study.

In thin section minnesotaite is transparent, clear and non-pleochroic. It is much coarser than greenalite, but generally not as tabular and chunky as the associated stilpnomelane sheaves. Minnesotaite sprays and rosettes have been found to cut across greenalite, stilpnomelane and carbonates. No distinct difference in composition was found among minnesotaites which texturally appear to have formed at the expense of earlier silicates (greenalite or stilpnomelane) or carbonates and chert.

Magnetite

Magnetite is present in all of the unleached assemblages of this study. Hematite was found only in a sample of Ruth Slate from the Schefferville mining area, where the rocks are locally highly oxidized and leached (analysis 8, Table 1). With electron microprobe techniques the variation in very small amounts of elements such as Mg, Al, Ti and Mn could not be established with confidence. In magnetite-manganoan carbonate (dolomite, ankerite or siderite) assemblages the MnO content of magnetite was found to be only 0.04 wt. %. MgO, Al_2O_3 and TiO_2 were found to be 0.02, 0.02 and 0.03 wt. % respectively. Magnetite, therefore, appears to be essentially pure Fe_3O_4 in these iron-formation assemblages.

In thin section, all magnetite occurrences exhibit features of recrystallization, ranging from very fine-grained to coarse-grained octahedral crystals with well-developed crystal outlines against coexisting minerals such as greenalite and recrystallized carbonates.

Chert or quartz

The grain size of the SiO_2 phase ranges from submicroscopic in some cements around granules to medium- to coarse-grained in fully recrystallized SiO_2-rich bands. No specific grain size measure was used to differentiate chert from quartz. When the grains appear as very fine-grained under high magnification it is referred to as chert; when coarser grain sizes are noted it is stated to be quartz.

Quartz or chert are found as thin bands interlayered with magnetite, Fe-silicates and carbonates, as granules and oolites, as regions in complex silicate-carbonate-chert granules, and as cements about granules and oolites.

Members of the dolomite-ankerite series

Members of this carbonate series are about as abundant as siderite in these iron-rich rocks. Ankerite-type compositions are more common in these occurrences than the generally Mn-rich dolomites. Representative analyses of members of the dolomite-ankerite series are given in Table 5. The most magnesian dolomite found contains 14.90 wt. % MgO and 8.67 wt. % MnO. MnO in dolomite ranges from 2.51 to 13.37 wt. %. Ankerites range up to a maximum of 22.77 wt. % FeO and show a range in MnO from 1.25 to 4.63 wt. %. Many of the dolomites and ankerites coexist with siderite, and such pairs are shown in Figure 2. The element fractionation between the carbonates (Fig. 3), and therefore the tieline slope between coexisting pairs, is very similar to that presented by French (1968) for the unmetamorphosed and essentially unaffected (French's Zones 1 and 2) parts of the Biwabik Iron Formation. It should be noted that the bulk chemical analyses (Table 1) of unaltered Sokoman Formation show a range from only 0.15 to 1.78 wt. % MnO. All Mn must

TABLE 5. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF MEMBERS OF THE DOLOMITE-ANKERITE SERIES

	1	2	3	4	5	6	7
FeO	5.03	5.90	6.07	11.19	22.77	15.61	16.20
MnO	10.30	8.00	9.08	2.51	1.25	3.57	3.25
MgO	11.18	11.88	12.39	12.24	6.33	7.27	6.86
CaO	29.01	31.29	33.15	29.73	26.80	26.79	26.88
CO_2†	44.48	42.93	39.31	44.33	42.85	46.76	46.81
Total	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)
	Recalculated on the basis of 2(Fe,Mn,Mg,Ca)						
Fe	0.139	0.157	0.152	0.304	0.654	0.469	0.490
Mn	0.288	0.215	0.231	0.069	0.036	0.109	0.100
Mg	0.549	0.563	0.553	0.592	0.324	0.390	0.370
Ca	1.025	1.065	1.064	1.035	0.986	1.032	1.041

†CO_2 obtained by subracting electron microprobe total from 100%

1,2,3. D.D.H. 1039D, depth 186'. No. 1 is central, fine-grained, somewhat cloudy part of manganoan dolomite oolite. No. 2 is clear, outer edge of same manganoan dolomite oolite. Analysis of siderite patches within this oolite is given in Table 6, anal. 6. No. 3 is clear, outer edge of complex dolomite oolite which encloses fine-grained stilpnomelane and greenalite.

4. D.D.H. 1039D, depth 130'. Clear, euhedral, medium- to coarse-grained dolomite coexisting with greenalite and magnetite.

5. D.D.H. 1032D, depth 183'. Clear, transparent, medium-grained, recrystallized ankerite, coexisting with stilpnomelane, siderite, greenalite and magnetite. (Stilpnomelane analysis in Table 3, no. 7; siderite analysis in Table 6, no. 1; greenalite analysis in Table 2, no. 5).

6,7. D.D.H. 1039D, depth 130'. No. 6 is clear, fine- to medium-grained mixture of granular ankerite and siderite, cementing composite ankerite and greenalite oolites and granules (see Table 6, no. 2 for siderite analysis). No. 7 is ankerite granule.

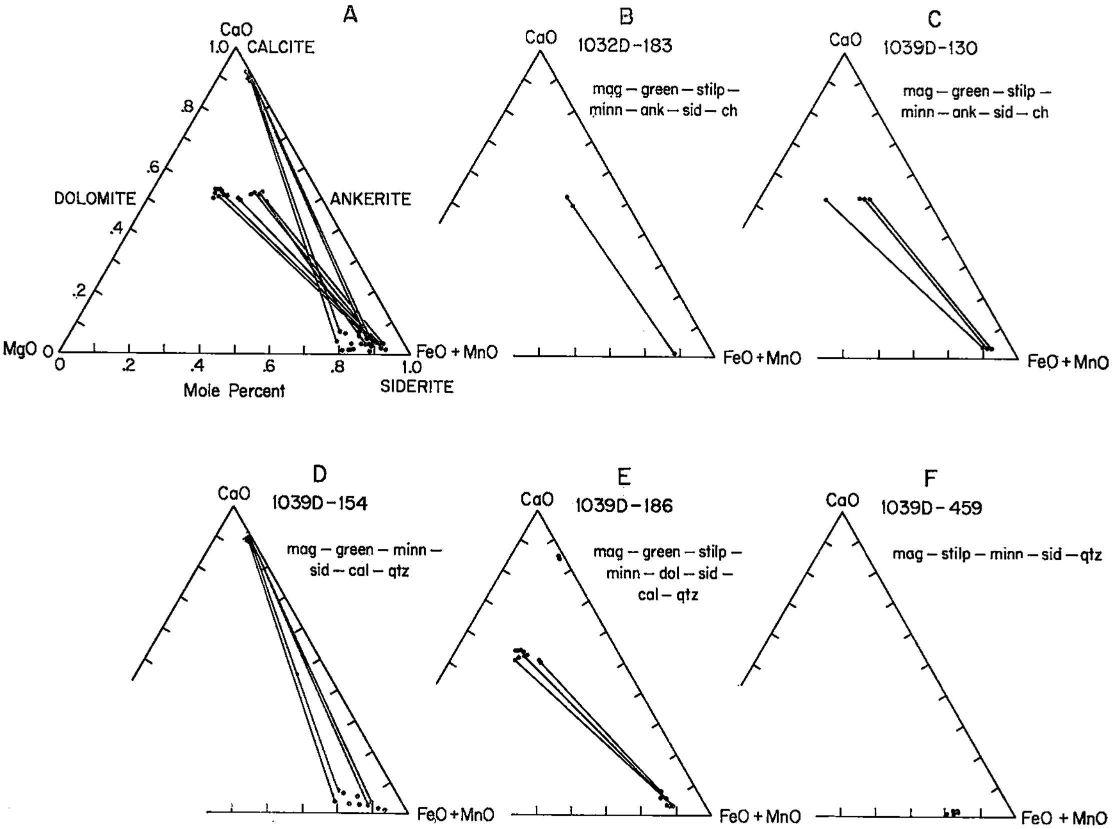

FIG. 2. Compositions of carbonates in silicate-rich horizons of the Sokoman Formation in the Howells River area, Labrador, Newfoundland, Canada. A. Composite diagram of all carbonate compositions in five different silicate-rich assemblages. Tielines connect coexisting (physically touching) carbonates. B. to F. Carbonate compositions of individual assemblages. Tielines connect physically touching carbonate pairs. Abbreviations are as follows: mag — magnetite; green — greenalite; stilp — stilpnomelane; minn — minnesotaite; ank — ankerite; sid — siderite; cal — calcite; ch — chert; qtz — quartz.

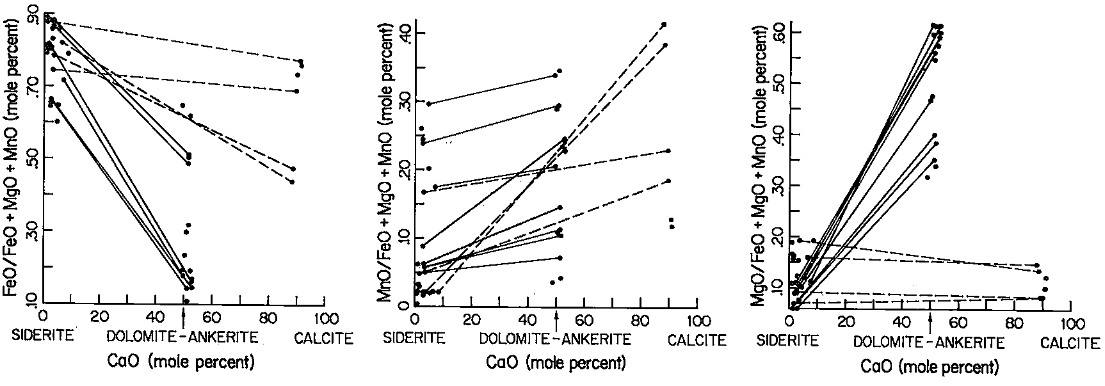

FIG. 3. Fe, Mn and Mg fractionation among the carbonates shown in Figure 2A. Tielines connect coexisting (physically touching) carbonate pairs.

TABLE 6. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF SIDERITE

	1	2	3	4	5	6	7	8	9	10
FeO	54.24	50.48	54.53	44.20	53.54	38.59	37.74	36.03	50.62	50.04
MnO	0.23	3.27	3.76	9.38	3.75	15.48	13.61	17.58	1.28	1.97
MgO	3.80	2.58	2.15	3.06	2.09	3.14	3.98	3.50	6.80	5.48
CaO	0.45	1.75	1.65	1.53	0.56	1.09	2.46	2.33	0.42	0.65
CO_2†	41.28	41.92	37.91	41.83	40.06	41.70	42.21	40.56	40.88	41.86
Total	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)	(100.00)
Recalculated on the basis of 2(Fe,Mn,Mg,Ca)										
Fe	1.755	1.665	1.697	1.436	1.733	1.260	1.222	1.143	1.568	1.598
Mn	0.008	0.109	0.119	0.323	0.123	0.512	0.446	0.565	0.040	0.064
Mg	0.219	0.152	0.119	0.177	0.121	0.183	0.230	0.198	0.376	0.312
Ca	0.019	0.074	0.066	0.064	0.023	0.046	0.102	0.095	0.017	0.027

†CO_2 obtained by subtracting electron microprobe total from 100%

1. D.D.H. 1032D, depth 183'; coarse-grained, recrystallized siderite in siderite-ankerite-stilpnomelane-greenalite-magnetite-chert assemblage (see Table 3, no. 7 for stilpnomelane analysis; Table 5, no. 5 for ankerite analysis; Table 2, no. 5 for greenalite analysis).

2,3. D.D.H. 1039D, depth 130'. No. 2 is recrystallized, euhedral siderite cementing ankerite granules and oolites (see Table 5, no. 6 for ankerite analysis). No. 3 is recrystallized, medium-grained euhedral siderite cementing complex granules consisting of greenalite, ankerite, and minnesotaite (for ankerite analysis see Table 5, no. 7, and see Fig. 11B).

4,5. D.D.H. 1039D, depth 154'. No. 4 is siderite in coarsely recrystallized siderite-calcite assemblage (see Table 7, no. 2 for calcite analysis; see also Fig. 11A). No. 5 is recrystallized siderite on outer edge of greenalite granules, cemented by similar siderite (see Table 2, no. 7 for greenalite analysis).

6,7,8. D.D.H. 1039D, depth 186'. No. 6 is fine-grained, euhedral siderite regions in Mn-rich dolomite oolites (for dolomite analyses see Table 5, nos. 1,2,3, and see Fig. 10C). Nos. 7 & 8 are similar siderite segregations inside dolomite oolites.

9,10. D.D.H. 1039D, depth 459'. No. 9 is medium-grained, recrystallized siderite in finely banded stilpnomelane-siderite-magnetite assemblages (see Table 3, no. 10 for stilpnomelane analysis). No. 10 is medium-grained siderite in thin siderite-magnetite-minor stilpnomelane bands.

be concentrated in dolomite, ankerite and siderite as none of the other coexisting phases contain significant MnO. Perrault (1955) concluded that ferroan dolomite + siderite compatibilities are common in many members of the Sokoman Formation.

Dolomite generally makes up the major part of the well-rounded carbonate oolites (Figs. 10A, 10B). The central, somewhat cloudy parts have more Mn and somewhat less Mg than the more transparent, clear outer edges of the same oolites (analyses 1 and 2, Table 5). These same oolites show discontinuous, unevenly distributed regions of siderite which are subparallel to the concentric banding of the oolites (Fig. 10C). Ankerite occurs in medium- to coarse-grained recrystallized, subhedral grains often in a mosaic intergrowth with medium-grained siderite (Fig. 11A). Such occurrences are especially common in thinly banded magnetite-stilpnomelane-ankerite-siderite-chert assemblages.

Siderite

Siderite is common in the silicate-rich members of the Sokoman Formation. It is about as abundant as members of the dolomite-ankerite series in most of the samples of this study. Representative analyses of siderite are given in Table 6. MnO in siderite ranges from 0.23 to 17.58 wt. %, MgO from 2.09 to 6.80 wt. % and CaO from 0.45 to 3.85 wt. %. As in the case of members of the dolomite-ankerite series, siderite houses large amounts of MnO whereas the other coexisting phases show insignificant MnO contents.

Siderite occurs as fine- to medium-grained euhedral regions distributed along concentric patterns in dolomite oolites as well as in medium- to coarse-grained mosaic intergrowths with ankerite in finely banded magnetite- carbonate-stilpnomelane-greenalite assemblages.

Calcite

Calcite in these iron-formation assemblages is by far the least abundant carbonate. Representative analyses are given in Table 7. FeO in calcite ranges from 4.33 to a maximum of 5.46 wt. % in a calcite coexisting with siderite. MnO ranges from 0.82 to 4.07 wt. % and MgO ranges from 0.37 to 0.72 wt. %.

In the only two assemblages (1039D-154 and 1039D-186) in which calcite was noted, it occurs as sporadic, fine- to medium-grained cement interlayered with greenalite cement between granules and oolites (Fig. 10D) or as medium- to coarse-grained recrystallized equigranular grains coexising with siderite in carbonate-greenalite-minnesotaite bands. Perrault (1955) reports that calcite is a minor constituent of the silicate-

TABLE 7. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF CALCITE

	1	2	3
FeO	5.51	5.46	5.46
MnO	1.38	1.80	0.90
MgO	0.35	0.37	0.41
CaO	52.51	53.19	53.29
CO_2†	40.25	39.18	39.94
Total	(100.00)	(100.00)	(100.00)

Recalculated on the basis of 2(Fe,Mn,Mg,Ca)	1	2	3
Fe	0.147	0.144	0.145
Mn	0.037	0.048	0.024
Mg	0.017	0.017	0.019
Ca	1.799	1.791	1.812

†CO_2 obtained by subtracting microprobe total from 100%

1&2. D.D.H. 1039D, depth 154'. No. 1 is medium-grained calcite covering greenalite, both cementing greenalite, minnesotaite, and magnetite granules (see Fig. 10D). No. 2 is coarse-grained calcite coexisting with siderite (see Fig. 11A, and analysis 4, Table 6).

3. D.D.H. 1039D, depth 186'. Coarse-grained, recrystallized calcite cementing (with greenalite) oolites composed of dolomite and siderite (see Tables 5 and 6 for analyses)

carbonate iron-formation in the Howells River area, but Zajac (1972) does not report calcite in his study of the Sokoman Formation in the Schefferville area. It clearly is an uncommon carbonate species in these iron-formation assemblages. French (1968), in his detailed optical and *x*-ray diffraction study of the carbonates of the Biwabik Iron Formation, concludes that calcite is absent in unmetamorphosed assemblages (French's Zone 1). Very minor and sporadic amounts as observed here by electron probe analysis can, however, be missed easily by optical and *x*-ray techniques.

Riebeckite

No riebeckite, or its fibrous variety, crocidolite, has been found in the Sokoman Formation in the Howells River area. Crocidolite-magnetite-quartz schists, however, are sporadically present in the Schefferville region in the lower red cherty (LRC) and pink grey cherty (PGC) horizons (Zajac 1972). In contrast, crocidolite can be a major constituent of the Precambrian iron-formations in Australia (*e.g.* Trendall & Blockley 1970) and South Africa (*e.g.* Peacock 1928). In the Walthier Lake area, bands of interlayered magnetite-crocidolite-quartz up to 75′ thick and 400′ wide are found in the silicate-carbonate iron-formation member (SCIF) of the Sokoman Formation (Richard E. Arndt, personal communication). One specimen from this occurrence was analyzed (no. 6, Table 1) and studied in detail. In it, fibrous, blue riebeckite (cross-fiber) occurs in bands up to 1 cm thick, interlayered between quartz-magnetite bands. In thin section the riebeckite is found to be finely interbanded with stilpnomelane-rich bands. The riebeckite is pleochroic from almost colourless to greenish-blue and the stilpnomelane varies from very light yellow to medium brown. Analyses of the two minerals are given in Table 8 (no. 5) and Table 3 (no. 5). Representative crocidolite analyses from Australian and South African iron-formation occurrences are given in Table 8, as well as an analysis for crossite (or ferroglaucophane, depending on the Fe^{2+}/Fe^{3+} ratio) from a crossite-stilpnomelane assemblage in the Franciscan Formation, California. Crocidolite analyses from iron-formations (Table 8, nos. 1-5) are remarkably similar except for some variations in MgO content. The crossite analysis from the Franciscan Formation (Table 8, no. 6) is much higher in Al_2O_3, and lower in total Fe. It is noteworthy that the bulk

TABLE 8. REPRESENTATIVE COMPLETE ANALYSES AND ELECTRON MICROPROBE ANALYSES OF CROCIDOLITE AND RIEBECKITE

	1	2	3	4	5	6
SiO_2	53.66	53.52	51.94	54.14	54.64	53.73
TiO_2	0.02	n.d.*	---	0.07	0.11	0.02
Al_2O_3	0.08	0.41	0.20	0.26	0.46	8.91
Fe_2O_3	17.73	17.72	18.64	21.07	29.35†	21.10†
FeO	14.67	16.26	19.39	9.27		
MnO	0.07	0.01	---	0.06	0.05	0.34
MgO	4.54	3.63	1.37	7.39	7.06	4.68
CaO	0.23	0.08	0.19	0.11	0.12	0.14
Na_2O	5.01	5.57	6.07	5.1	5.91	7.56
K_2O	0.07	0.05	0.04	0.00	0.01	0.01
$H_2O(+)$	2.81	2.63	2.58	2.02		
$H_2O(-)$	0.33	0.32	0.31	0.02	(2.29)††	(3.51)††
F	---	---	---	0.09		
Total	99.22**	100.20**	100.73	99.60	(100.00)	(100.00)

Recalculated on the basis of

	1		2		3		4				5		6	
	24(O,OH)		24(O,OH)		24(O,OH)		24(O,OH,F)		23 oxygens		23 oxygens		23 oxygens	
Si	7.993	8.00	7.976	8.00	7.879	7.91	7.956	8.00	8.380	8.38	8.310	8.31	7.940	8.00
Al	0.007		0.024		0.035		0.044		0.000		0.000		0.060	
Al	0.007		0.049		0.000		0.001		0.047		0.082		1.492	
Ti	0.002		0.000		0.000		0.008		0.008		0.013		0.002	
Fe^{3+}	1.987		1.987		2.127		2.330		3.657†		3.733†		2.608†	
Fe^{2+}	1.828		2.023		2.460		1.139							
Mn^{2+}	0.009	6.34	0.001	6.50	0.000	6.72	0.007	6.57	0.008	6.97	0.006	7.20	0.043	7.36
Mg	1.008		0.806		0.309		1.619		1.705		1.600		1.031	
Ca	0.037		0.012		0.031		0.017		0.018		0.020		0.022	
Na	1.446		1.611		1.786		1.453		1.530		1.742		2.166	
K	0.014		0.010		0.008		0.000		0.000		0.002		0.002	
OH	2.793		2.614		2.619		1.978	2.02						
F							0.042							

n.d.* none detected --- not determined †total Fe recalculated as FeO only ††H_2O values in brackets obtained by subtracting microprobe total from 100 %

**additional components in column 1: P_2O_5 0.36, CO_2 0.57, FeS_2 0.02 wt. %, making total 100.17. In column 2, P_2O_5 0.20 wt. %, making total 100.40.

1. Crocidolite, iron-formation of the Hamersley Group, Australia (Trendall & Blockley 1970). 2. Massive riebeckite, iron-formation of the Hamersley Group, Australia (Trendall & Blockley 1970). 3. Crocidolite in crocidolite-magnetite-quartz assemblage from iron-formation near Kliphuis, South Africa (Peacock 1928).
4. Crocidolite from crocidolite-magnetite-chert assemblage in the Sokoman Formation, Knob Lake area, Quebec and Newfoundland (Zajac 1972). 5. Walthier Lake area, 23 miles NW of Schefferville, Quebec; stilpnomelane riebeckite (crocidolite)-magnetite-quartz assemblage (see Table 3, no. 5 for anal. of coexisting stilpnom.)
6. Franciscan Formation in Laytonville Quarry, Mendecino County, California; crossite (or ferroglaucophane depending on ferrous-ferric ratio) in crossite-stilpnomelane-quartz schist (metachert of Chesterman 1966). See Table 3, no. 6 for analysis of coexisting stilpnomelane.

chemical analyses for the crocidolite- and crossite-bearing host rocks show Na_2O contents of 2.95 and 0.75 wt. % respectively (Table 1, no. 5 and footnote no. 6 of Table 3). This Na_2O is concentrated almost exclusively in the Na-amphibole as the Na_2O values for the coexisting stilpnomelane are only 0.08 and 0.02 wt. % (Table 3, nos. 5 and 6). Stilpnomelane analyses 7 to 10 (Table 3), however, show Na_2O values ranging from 0.15 to 0.42 wt. %.

The complete chemical analyses quoted from the literature in Table 8 were recalculated on the basis of 24(O,OH), except for analysis no. 4 which was also recalculated on the basis of 23 oxygens as was done for the electron microprobe data. Comparison of the two recalculation schemes for analysis no. 4 shows that the assumption of total Fe as Fe^{2+} only, can lead to large errors in cation numbers and cation site assignments when Fe^{3+} is high. The cation recalculations of analyses 5 and 6 are, therefore, approximate at best.

The crocidolite occurrences in the Sokoman Formation have textures which reflect strong shearing, crenulation, and deformation. Such deformational textures are absent in the rocks of the Howells River area. Although strong structural metamorphic effects are clearly visible in the Schefferville region and are virtually absent in the Howells River area, there is no evidence to suggest that the low-temperature, thermal regimes were much different in the two regions.

TEXTURAL RELATIONS

The Sokoman Formation in the Howells River area is especially well-suited for a study of possible primary, as well as diagenetic and low-grade metamorphic textures. Although sedimentary features such as very fine banding, granular and oolitic textures are very well preserved, all of the assemblages show the effect of a very low-grade metamorphic overprinting. This allows for the possible deduction of reaction sequences among the carbonates, Fe-silicates and chert.

Greenalite occurs typically in very fine grain size in somewhat ellipsoidal granules and more rarely in thinly banded oolites (Figs. 4A, B). The layering in the oolites is shown by finely alternating dark green and brownish-green banding. Greenalite is found also as a cement around granules and oolites (Fig. 4C). These greenalite cements are generally somewhat lighter green than the greenalite of the granules and oolites, but no distinctive difference in composition was found between them. In addition, greenalite occurs as massive thin bands up to 0.5 cm thick. The bands parallel the very fine, well-preserved banding common in some greenalite-magnetite-chert-carbonate assemblages (Fig. 4D). Less commonly, greenalite is found as angular and broken fragments concentrated in bands parallel to the chert-magnetite banding of the host rock (Fig. 5B). Large composite carbonate granules often enclose greenalite granules (Fig. 5C). The greenalite matrix of some larger granules appears to have cracked, possibly due to shrinkage caused by dehydration of a precursor of greenalite-type composition (Fig. 5A).

In many occurrences greenalite is so fine-grained that, in places, it appears almost isotropic under doubly polarized light. In some thicker greenalite bands, almost isotropic bands alternate with greenalite bands having a slightly larger grain size (about one micron). These textural observations lead to the conclusion that greenalite is probably one of the earliest and still only very slightly recrystallized constituents of the iron-formation. In many occurrences, however, greenalite has not survived the low-grade metamorphic conditions and has reacted to form stilpnomelane or minnesotaite (Fig. 5D) as discussed below.

Stilpnomelane is not as common as greenalite in the rocks of this study. In contrast to greenalite, stilpnomelane is generally medium-grained and occurs in well-crystallized sheaves, rosettes and irregular patches. It is not a major constituent of oolites or granules, but occurs frequently as irregular, well-crystallized patches within greenalite granules or bands (Fig. 6A). It commonly occurs in close association and mosaic textural intergrowth with magnetite and siderite in finely banded iron-formation (Fig. 6B). By far the most common stilpnomelane is highly pleochroic from light yellow to dark brown, indicating a considerable Fe^{3+} component. However, in a few assemblages a colourless to light green and a dark brown pleochroic variety of stilpnomelane adjoin each other. As no difference in composition between these two varieties was found by electron microprobe methods, their colour differences probably reflect differences in Fe^{2+}/Fe^{3+} ratios (Fig. 6C). It is concluded that these Fe^{2+}/Fe^{3+} variations reflect the oxidation state of original sedimentary precipitates, or diagenetic products, and that they are not the product of later oxidation. Stilpnomelane has never been found as a cement, as has greenalite, around granules and oolites. Much stilpnomelane has reacted to form later minnesotaite, as shown by the common cross-cutting relations of minnesotaite sprays and rosettes in medium-grained stilpnomelane (Fig. 6D). These textures suggest that

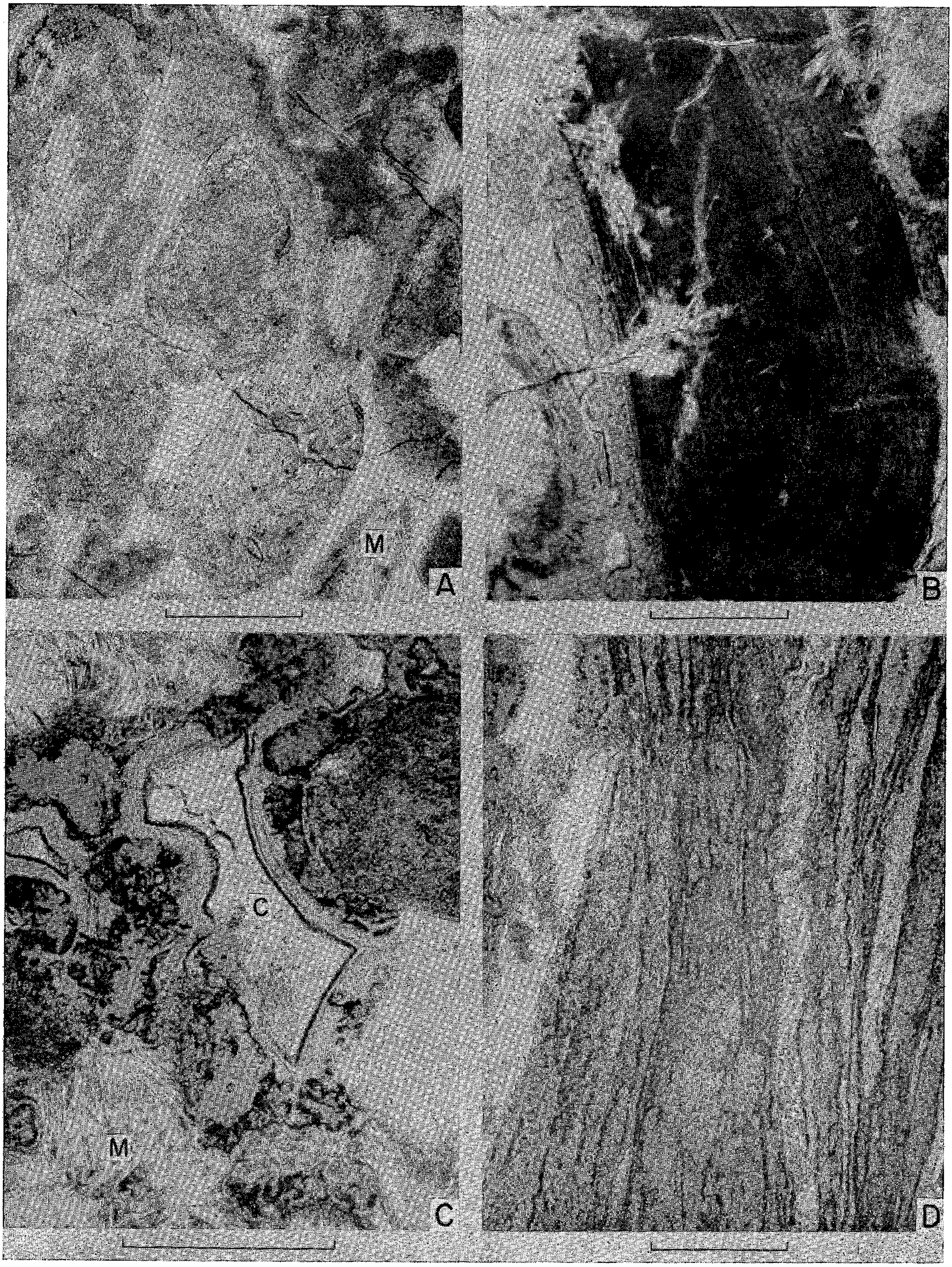

FIG. 4. Greenalite occurrences. A. Massive greenalite granules surrounded by chert (colourless) and minnesotaite (M). B. Greenalite oolite with fine banding; lighter greenalite cement at left. White patch in oolite is minnesotaite. C. Greenalite cementing greenalite granules. Cement interior is chert (C). White sprays are minnesotaite (M). D. Thinly banded greenalite; white bands at left are minnesotaite. Bar length represents 0.2 mm.

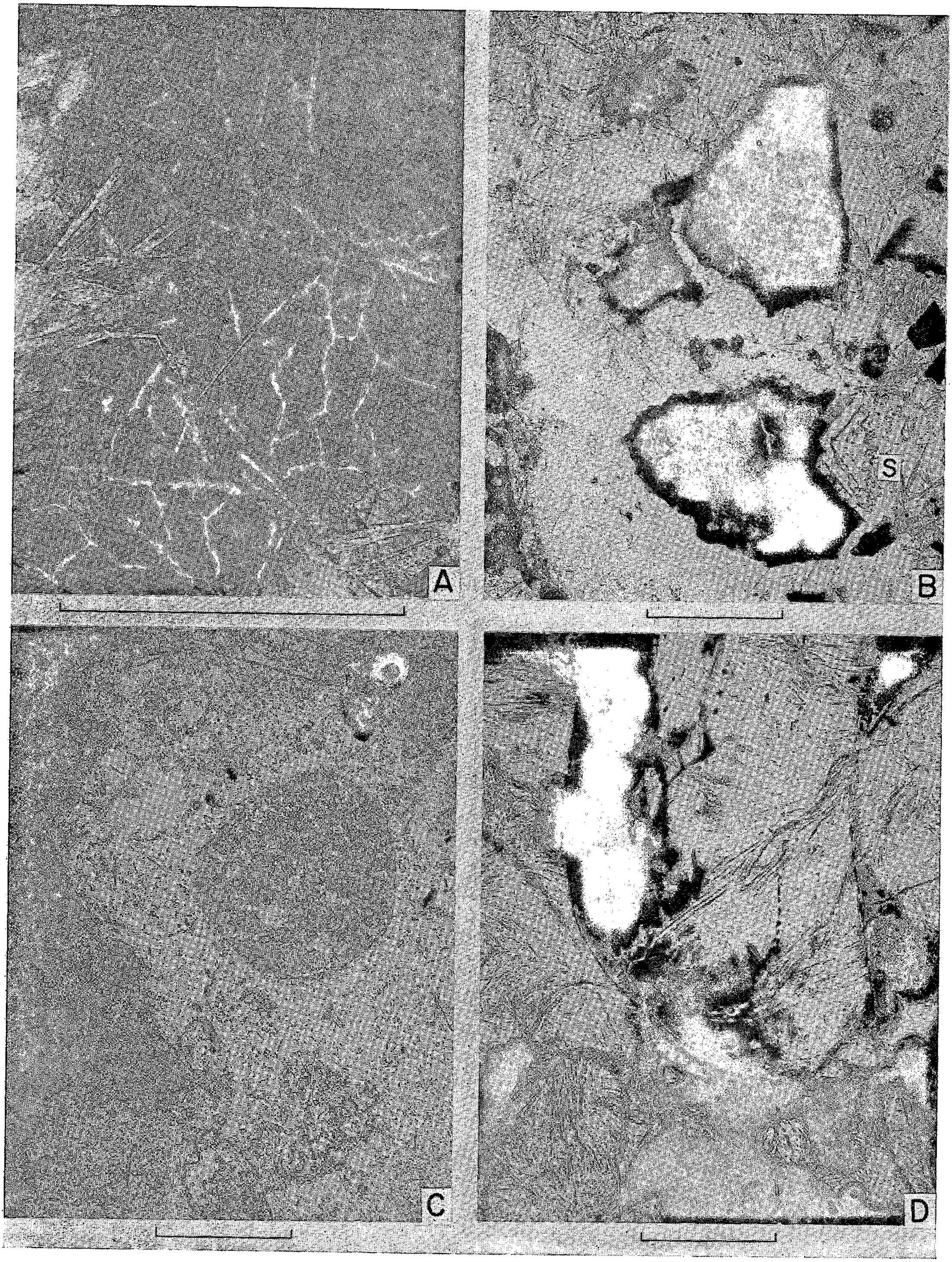

FIG. 5. Greenalite occurrences. A. Cracks, possibly due to shrinkage, in massive greenalite granule. Sprays are minnesotaite. B. Irregularly shaped fragments of greenalite (dark in colour) in chert matrix (clear, colourless). Siderite (S) rhombohedron at lower right. C. Small greenalite granule inside larger manganoan dolomite oolite. Greenalite cement at left. D. Relict outline of greenalite granules and oolites which now in large part consist of felted masses of minnesotaite (light coloured). Relict edges are commonly accentuated by fine stringers of magnetite at the outer edge of the granule. These may well be the result of greenalite reacting to form minnesotaite and magnetite (see Table 10). Bar length represents 0.2 mm.

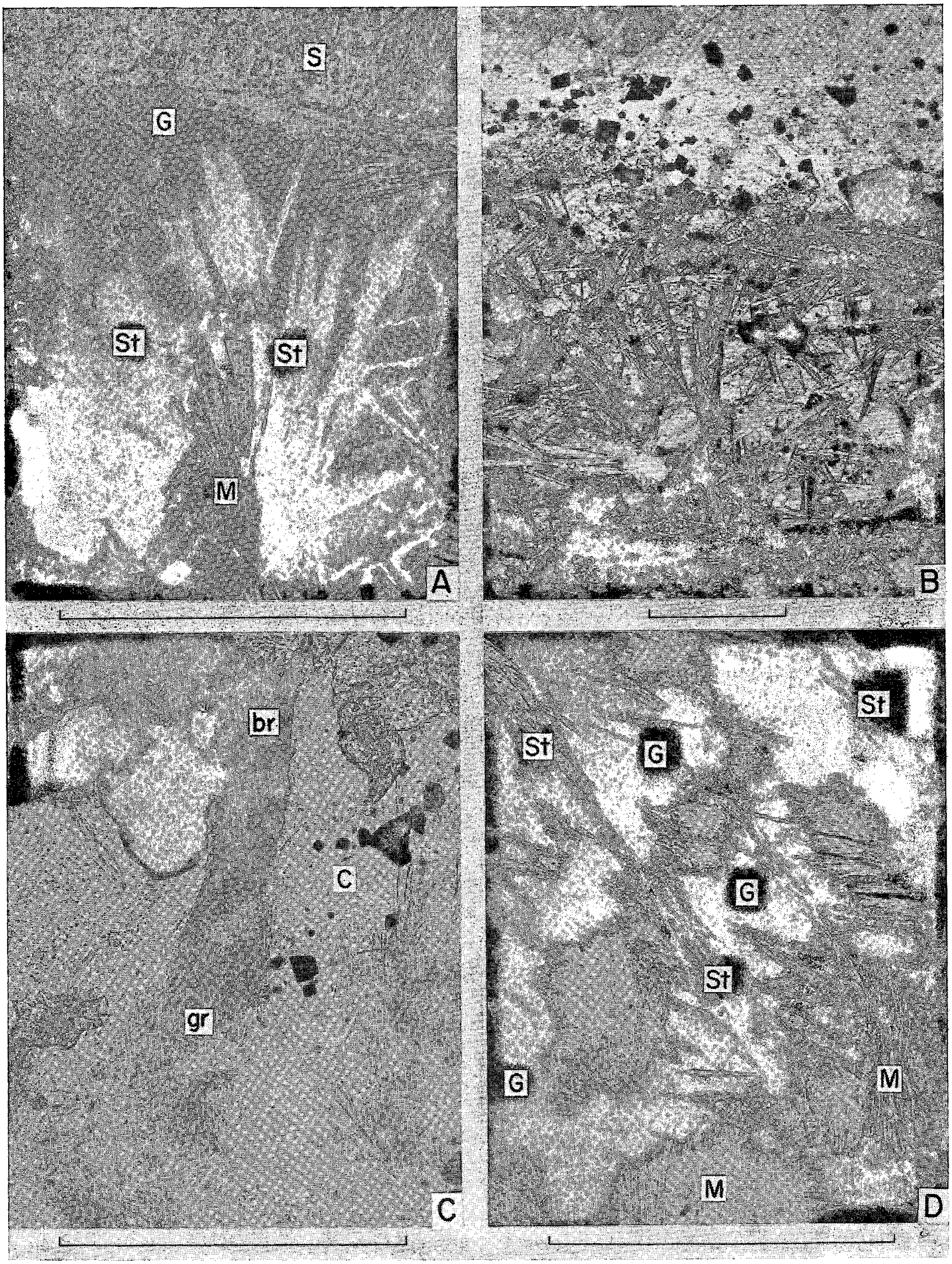

FIG. 6. Stilpnomelane occurrences. A. Dark brown highly pleochroic stilpnomelane (St) sprays inside greenalite (G). Siderite (S) at top. Minnesotaite (M) cross-cutting stilpnomelane. Opaque is magnetite. B. Stilpnomelane sprays (dark) in bands of magnetite-siderite-quartz. C. Coexistence of dark brown stilpnomelane (br) at top with light green stilpnomelane (gr) at bottom. Opaque is magnetite. Colourless, low relief mineral is chert (C). D. Well-crystallized dark brown sheaves of stilpnomelane (St) cross-cutting very fine-grained greenalite (G). The stilpnomelane in turn is cut by minnesotaite (M). Bar length represents 0.2 mm.

stilpnomelane is an early recrystallization and reaction product in greenalite-type matrices and in carbonate-magnetite-chert assemblages.

Minnesotaite is common in all silicate and carbonate assemblages of this study. It occurs as fine- to medium-grained sprays and rosettes and as massive bands (Figs. 7A, B). In some occurrences, as in the silicate-carbonate member (SCIF) of the Sokoman Formation (Table 1, no. 7), it makes up 95% or more of the whole rock (Fig. 7C). Here the original fine sedimentary banding, and possible granular or oolitic textures have been completely obliterated. In carbonate-rich occurrences minnesotaite shows cross-cutting relationships across carbonate grain boundaries and oolites (Fig. 7E).

From the cross-cutting relations of minnesotaite in greenalite, stilpnomelane, and carbonates it is concluded that minnesotaite is not primary but the result of a combination of diagenetic and very low-grade metamorphic reactions.

Magnetite. Although magnetite ranges from fine- to coarse-grained, its form is always euhedral (octahedral). Magnetite occurs most frequently in thin bands, interlayered with chert, carbonates and Fe-silicates (Figs. 8A, B). It also occurs in strongly recrystallized assemblages which show the relict outline of magnetite granules (Fig. 8C). In many assemblages it forms recrystallized rims around greenalite granules, in which the magnetite borders are medium- to coarse-grained, but the greenalite center shows its customary extremely fine grain size (Fig. 8D). Magnetite is the only Fe-oxide in the assemblages studied except for the hematite in a sample of the Ruth Slate.

Because magnetite always displays well-developed octahedral faces against the coexisting minerals, it is concluded to be the product of recrystallization during diagenesis and subsequent very low-grade metamorphism. The euhedral form is not regarded as the product of replacement of granules or granule edges, or thin bands in the iron-formation. French (1968, 1973) shows photomicrographs of occurrences very similar to the ones described here (*e.g.* French 1968, Fig. 11; reproduced in French 1973, as Fig. 9) but interprets them to be the result of magnetite replacing earlier silicate granules. Dimroth & Chauvel (1973) show photomicrographs and black-line drawings (their Figs. 8C and 11E) which are essentially identical to the photographs shown in Figure 8. They also interpret these textures as replacement of earlier materials by magnetite. Contrary to such textural interpretations, which are common in the literature on low-grade iron-formation (see French 1973 for a listing of authors and textural interpretations of assemblages in low-grade iron-formations), the author concludes that the euhedral outline of magnetite is the result of its recrystallization from earlier, undoubtedly less well-organized Fe_3O_4 or hydrous Fe^{2+}-Fe^{3+} oxides. Euhedral outline against coexisting minerals suggests a strong force of crystallization, but is by no means unambiguous evidence for replacement.

Quartz or chert are present in all assemblages as oolites or granules, as cements, and as finely granular, recrystallized bands and patches. Figure 9A shows the very common occurrence of granular quartz around relict granules and oolites, and Figure 9B shows chert cementing greenalite and chert granules. In some assemblages quartz veinlets are noted inside fractured granules and oolites, indicating some remobilization of SiO_2, probably during the continuous process from diagenesis to very low-grade metamorphism.

Carbonates are present in all of the unleached Fe-silicate-rich assemblages of this study. Calcite, the least common carbonate, occurs in two rather distinct textural modes. It is found as medium-grained cements around granules and oolites (Fig. 10D) and in medium- to coarse-grained intergranular mosaic intergrowths with siderite (Fig. 11A). As its occurrence is relatively sporadic it is not easily detected under the microscope.

Members of the dolomite-ankerite series occur in well-crystallized medium- to coarse-grained mosaic textures as a matrix for relict granules of chert and dolomite or ankerite, and in massive bands in silicate-carbonate assemblages. Manganiferous dolomites are the main constituent of recrystallized oolites (Figs. 10A to C) in which euhedral siderite patches outline the relict concentric banding of the oolites. These oolite occurrences are texturally very informative. The central parts of the oolites are generally finer-grained and somewhat cloudy, whereas the outer edges are coarser-grained and transparent. The outer parts of the oolites also show the siderite rhombohedra and patches most abundantly. Cementing materials around the oolites are greenalite and calcite. These oolites show only features of recrystallization, none of replacement. They are concluded to be the recrystallized products of a Ca-Fe-Mn-carbonate ooze, originally probably very fine-grained and poorly ordered. During diagenesis and subsequent very low-grade metamorphism the disordered carbonate material ordered itself and caused the phase separation (exsolution) of siderite from the Mn-dolomite matrix. Ankerites are medium- to coarse-grained, granular, and often

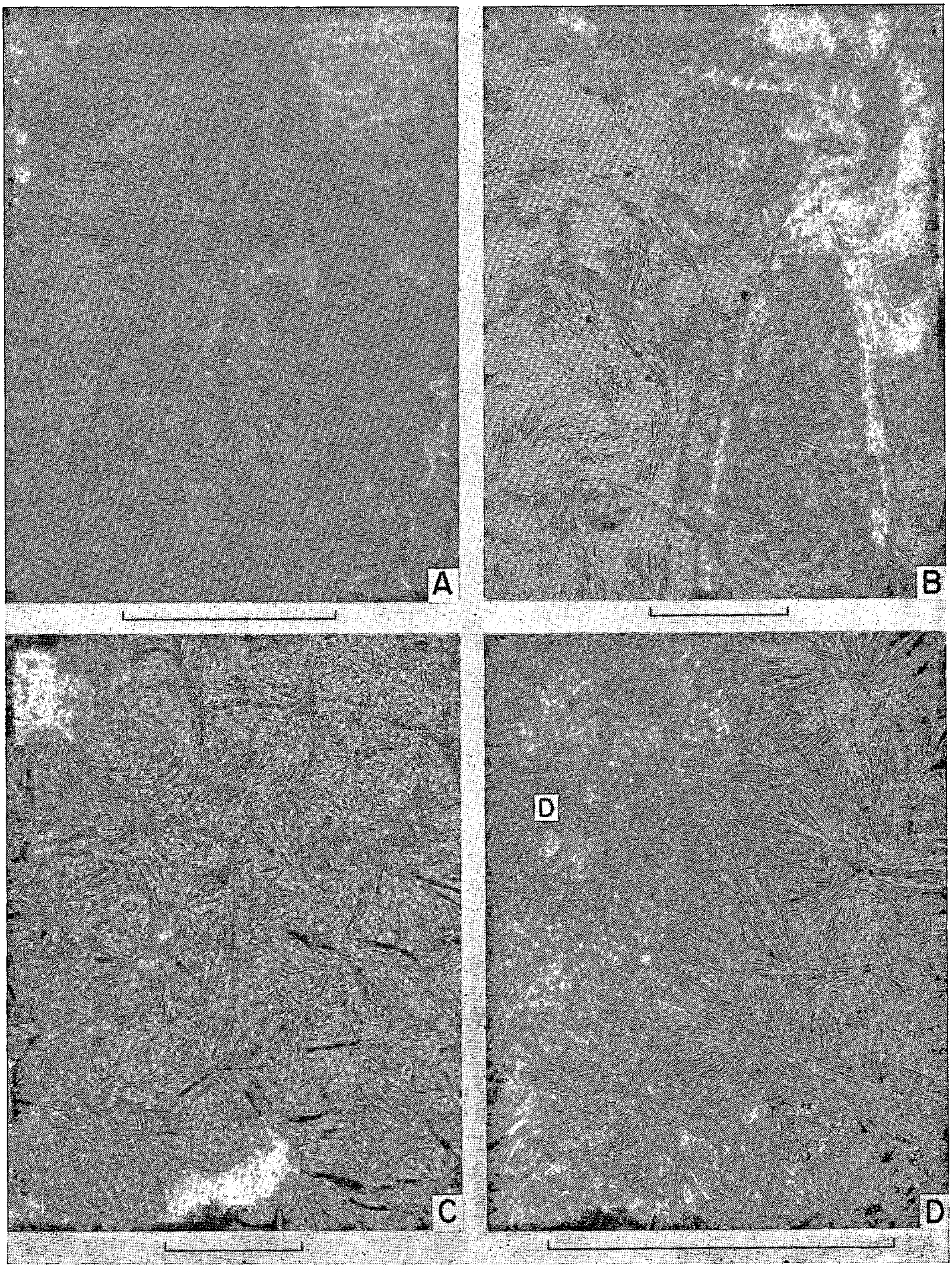

FIG. 7. Minnesotaite occurrences. A. Fine-grained minnesotaite sprays in matrix of fine-grained quartz. B. Minnesotaite masses in what originally had been greenalite granules. Relict edges of granules, and some greenalite cement (at right side) still remain. C. Felted masses of minnesotaite which have obliterated all original texture. D. Minnesotaite sprays cross-cutting the outer edge of a manganoan dolomite oolite. The central part of the oolite (D) is at the upper left. Bar length represents 0.2 mm.

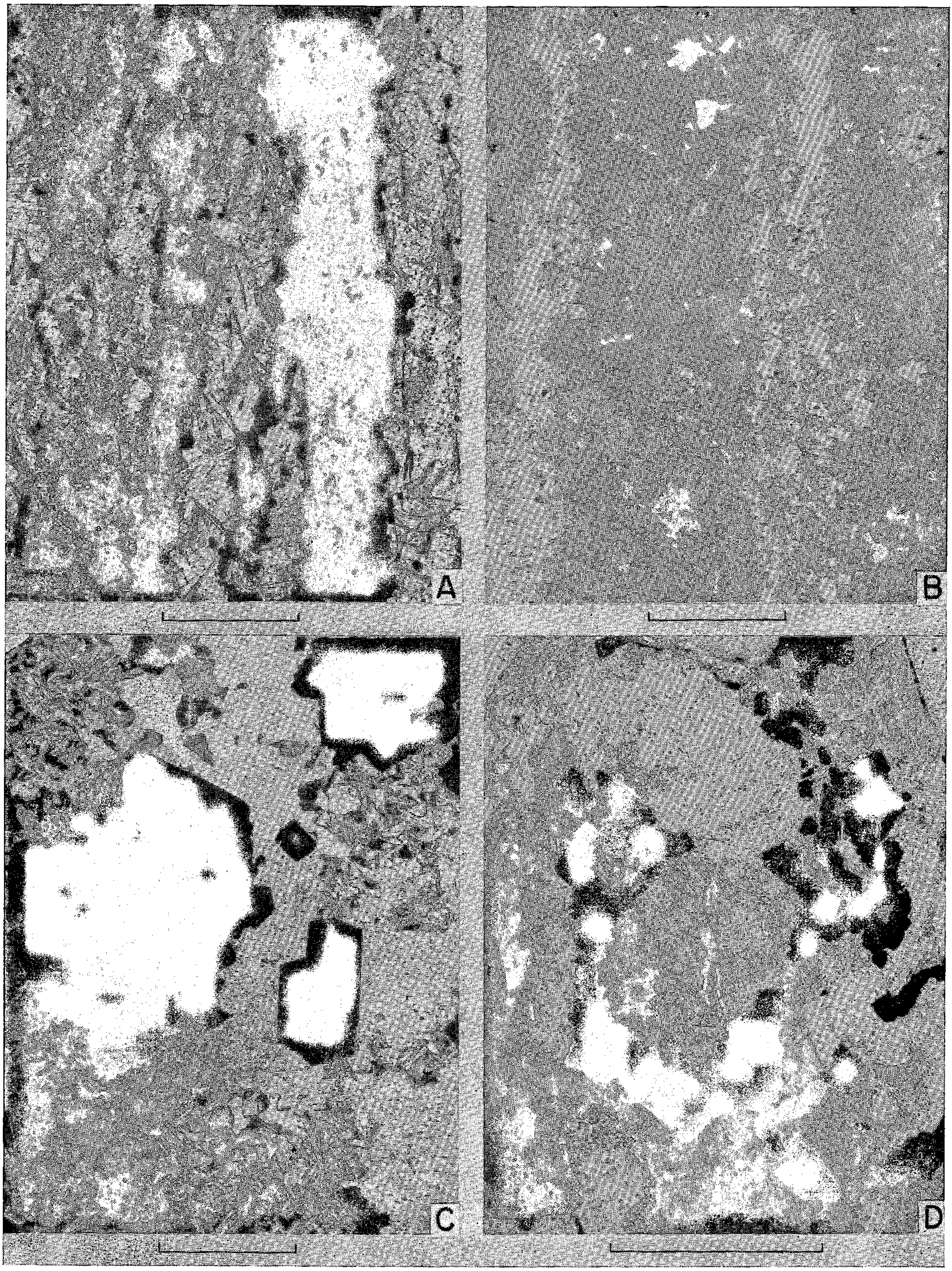

FIG. 8. Magnetite occurrences. A. Finely banded magnetite (black) - siderite-stilpnomelane iron-formation. B. Similar occurrence as in A, but in reflected light, showing euhedral outline of all magnetite grains. C. Coarsely recrystallized magnetite granules in siderite-quartz-minnesotaite matrix. Doubly polarized light. D. Greenalite granules with outer edges of magnetite. The greenalite is very fine-grained but the magnetite is recrystallized and euhedral. Bar length represents 0.2 mm.

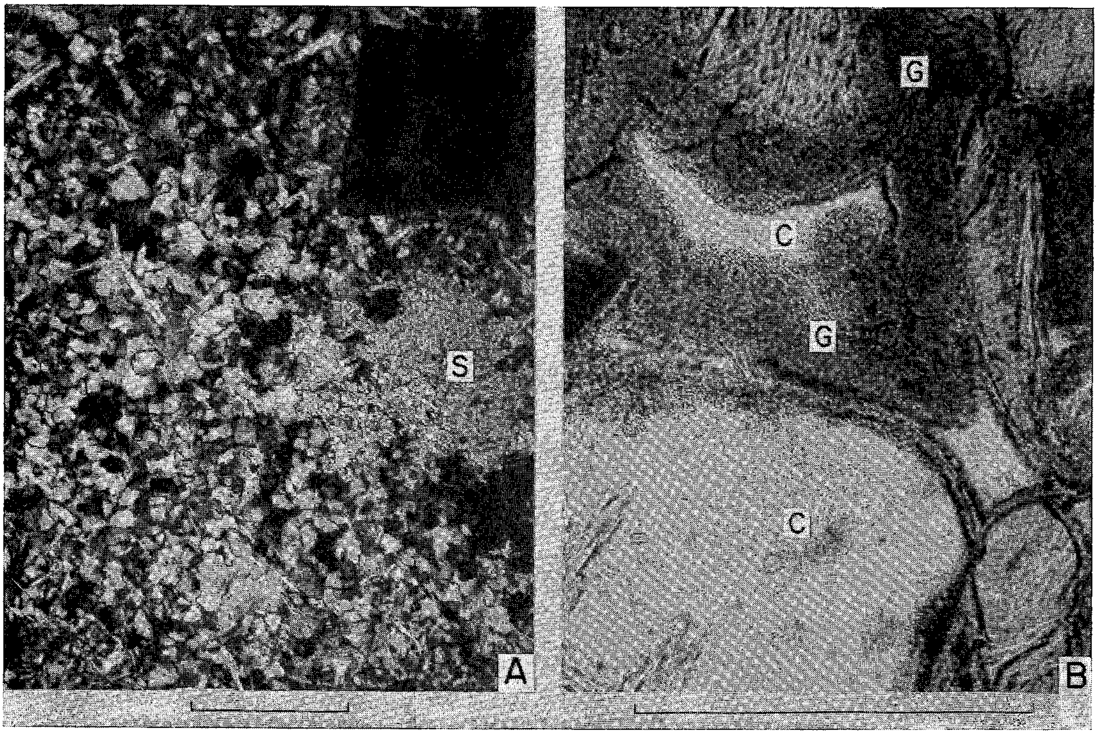

FIG. 9. Quartz and chert occurrences. A Fine-grained quartz matrix around relict siderite (S) granule. The siderite is medium-grained and well-crystallized. Opaque is magnetite. Doubly polarized light. B. Chert (C) and greenalite (G) cements surrounding greenalite and chert granules. Transparent sprays are minnesotaite. Bar length represents 0.2 mm.

much coarser than coexisting stilpnomelane and chert. The coarseness of ankerite is concluded to be the result of recrystallization, and associated diffusion of cations, during diagenesis and subsequent very low-grade metamorphism. Perrault (1955) suggests that these ferroan dolomites represent replacement of earlier materials. The present author concludes that the ankerites are the recrystallization products of earlier much finer-grained ankerite compositions.

Siderite is an abundant constituent of well-banded stilpnomelane-quartz-magnetite-siderite occurrences (Fig. 11C). Grain sizes in such occurrences can alternate abruptly from very fine to coarse granular siderite bands. The compositions of both types of siderite are essentially identical. As in the case of the other carbonate occurrences, the author considers siderite to be the medium- to coarse-grained recrystallization product of earlier much finer-grained material of siderite composition.

Crocidolite is not found in the Howells River area, but occurs in the structurally highly deformed area of Schefferville, and northwest thereof. Crocidolite occurrences are most notable in finely crenulated and sheared Na-rich rocks, providing conclusive evidence that crocidolite is a very low-grade metamorphic product of Na-rich bulk compositions. Dimroth & Chauvel (1973) and Zajac (1972) reached similar conclusions on the origin of the crocidolite in the Sokoman Formation. The coexistence of stilpnomelane and crocidolite (Fig. 11D) is evidence for an overlap of the very low-grade metamorphic stability fields of the two minerals.

PETROGENESIS AND CONCLUSIONS

The above textural observations enable interpretation of the possible primary, diagenetic and low-grade metamorphic iron-formation assemblages. The products of sedimentation were probably hydrous Fe-silicate gels of greenalite-type composition, locally hydrous Na-, K-, Al-rich iron-silicate gels approximating stilpnomelane compositions, SiO_2 gels (or magadiite, or a sodium silicate gel, as suggested by Eugster & Chou 1973), $Fe(OH)_3$ and $Fe(OH)_2$ precipitates, and very fine-grained carbonate oozes of variable composition. The possible products of sedi-

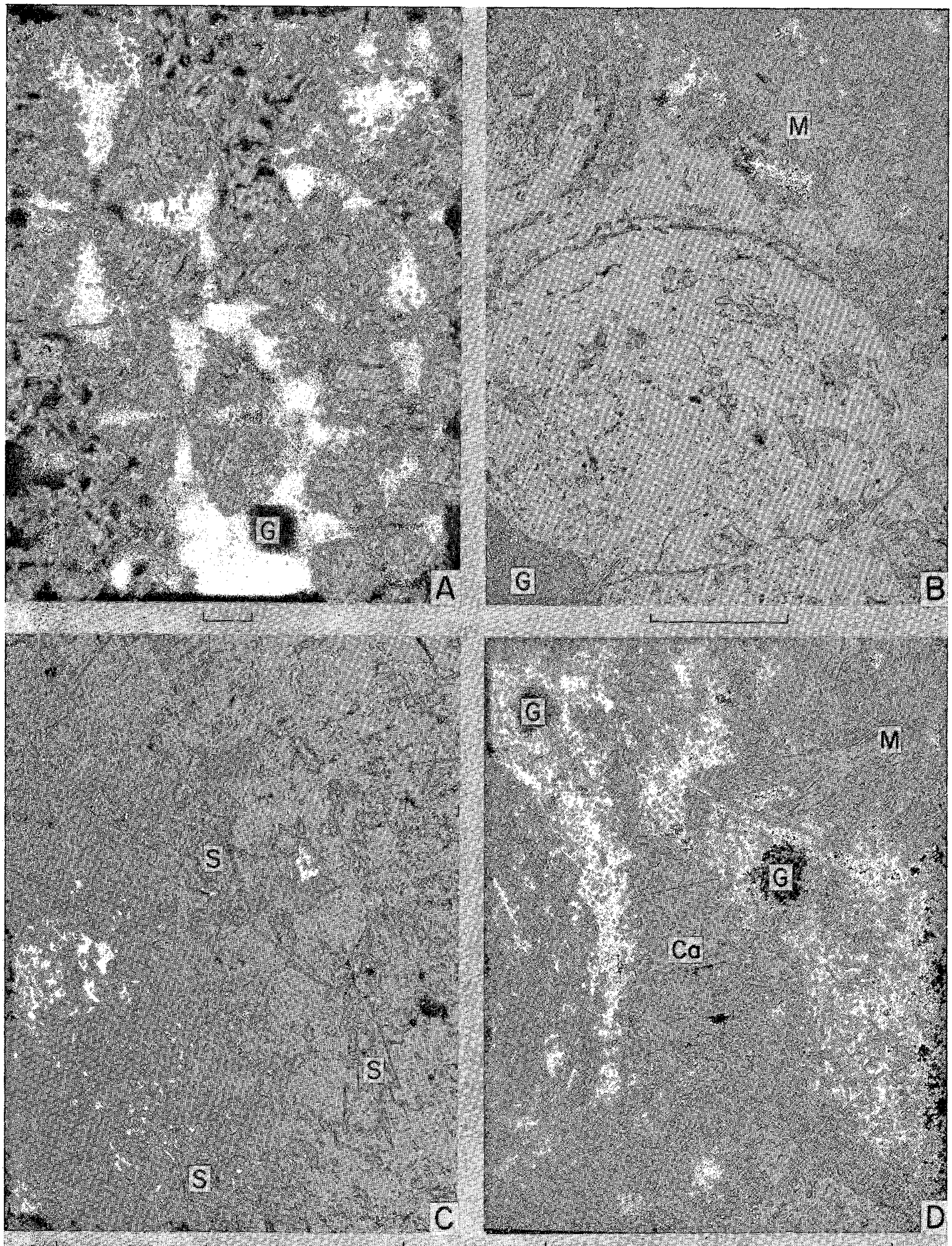

FIG. 10. Carbonate occurences. A. Manganoan dolomite oolites, in doubly polarized light, showing radial arrangement of dolomite crystallites. Black area is very fine-grained greenalite (G). B. Close-up of a dolomite oolite. Felted masses at upper right are minnesotaite (M). Greenalite at lower left (G). C. Close-up of siderite rhombohedra (S) inside oolite shown in B. The rhombohedra are concentrically arranged. D. Calcite (Ca) cement inside greenalite (G) cement around dolomitic oolites. Minnesotaite (M) at upper right. Bar length represents 0.2 mm.

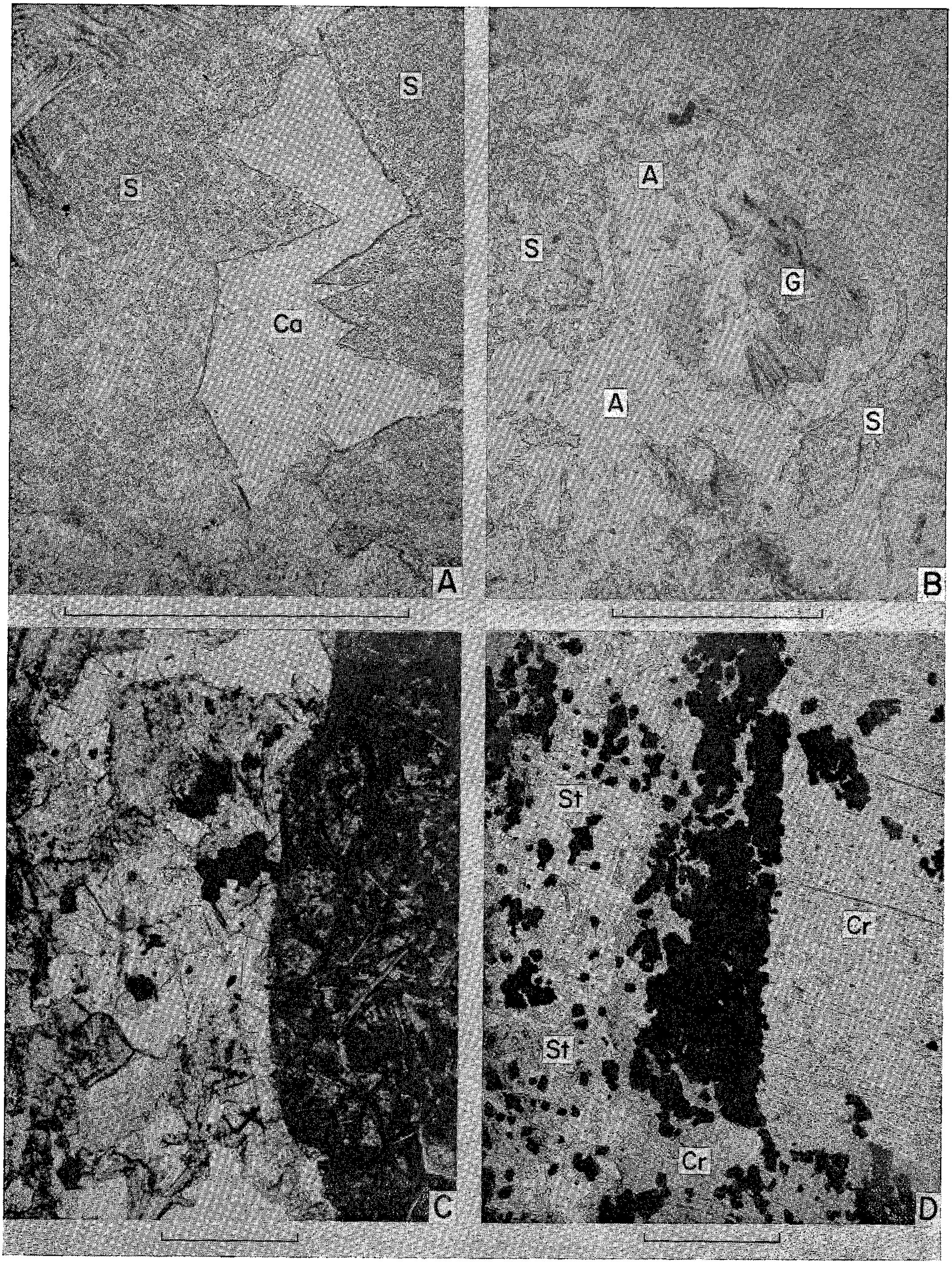

FIG. 11. Carbonate and riebeckite occurrences. A. Coexistence of medium-grained, euhedral siderite (S, with high relief) and subhedral calcite (Ca). B. Composite granule with greenalite (G) center, and ankerite edge (A), cemented by more ankerite (A) and siderite (S). C. Medium-grained, transparent siderite at left, and fine-grained siderite of similar composition at right, in finely banded magnetite-siderite assemblage. Sheaves in the right hand band are stilpnomelane. Opaque is magnetite. D. Coexistence of crocidolite (Cr, cross-fiber variety of riebeckite), stilpnomelane (St) and magnetite (opaque). Bar length represents 0.2 mm.

mentation are listed in Table 9 and a possible primary assemblage diagram is given in Figure 12A. During diagenesis H_2O is lost from the more open gel-type compositions due to compaction. Furthermore, the amorphous silicate gels probably become somewhat less disordered structures. For example, amorphous greenalite-type compositions may tend toward very fine-grained, somewhat ordered greenalite and hydrous Na-, K-, Al-rich iron-silicate gels may tend to acquire the structural arrangement of a possible precursor to stilpnomelane. The very fine-grained carbonate oozes would tend to recrystallize, as would very fine-grained magnetite-type compositions. A possible set of diagenetic assemblages is given in Figure 12B, showing the possible onset of minnesotaite formation. With a continuous increase in temperature, in going from diagenetic to very low-grade metamorphic conditions, stilpnomelane would tend to coarsen in grain size and chert would recrystallize. The carbonates would also coarsen in grain size and produce distinct phase separations across miscibility gaps (*e.g.* siderite-ankerite and calcite-siderite coexistences). Minnesotaite would form pervasively at the expense of earlier silicates (greenalite and stilpnomelane), and by the reaction of chert and Fe-carbonates. Reactions which may be responsible for the formation of minnesotaite, as deduced from textural evidence, are given in Table 10. An assemblage diagram for the very low-grade metamorphic products of iron-formation is given in Figure 12C. The trend, as expressed by the assemblage groupings in Figures 12A, B, and C, is one of decreasing H_2O content as would be expected in going from sedimentary to low-grade metamorphic products.

TABLE 9. INFERRED INITIAL COMPOSITIONS AND THEIR SEDIMENTARY PRODUCTS IN PRIMARY IRON-FORMATION ASSEMBLAGES

colloidal SiO_2	⟶	chert
dissolved SiO_2 + Fe^{2+},Mg	⟶	amorphous Fe-Si-O-OH gel of greenalite type
+		
locally Na^+, K^+, Al^{3+}	⟶	amorphous Fe-Si-O-OH-(Na,K,Al) gel of stilpnomelane type
dissolved Fe^{3+}	⟶	$Fe(OH)_3$ (becomes hematite)
+		
dissolved Fe^{2+}	⟶	$Fe(OH)_2$ + $Fe(OH)_3$ (becomes magnetite)
dissolved CO_2, Fe^{2+}, Mg, Ca	⟶	very fine-grained "mixed" carbonates

*chert may form from magadiite, $NaSi_7O_{13}(OH)_3 \cdot 3H_2O$, during diagenesis (Eugster & Chou 1973).

A chemically somewhat more realistic set of

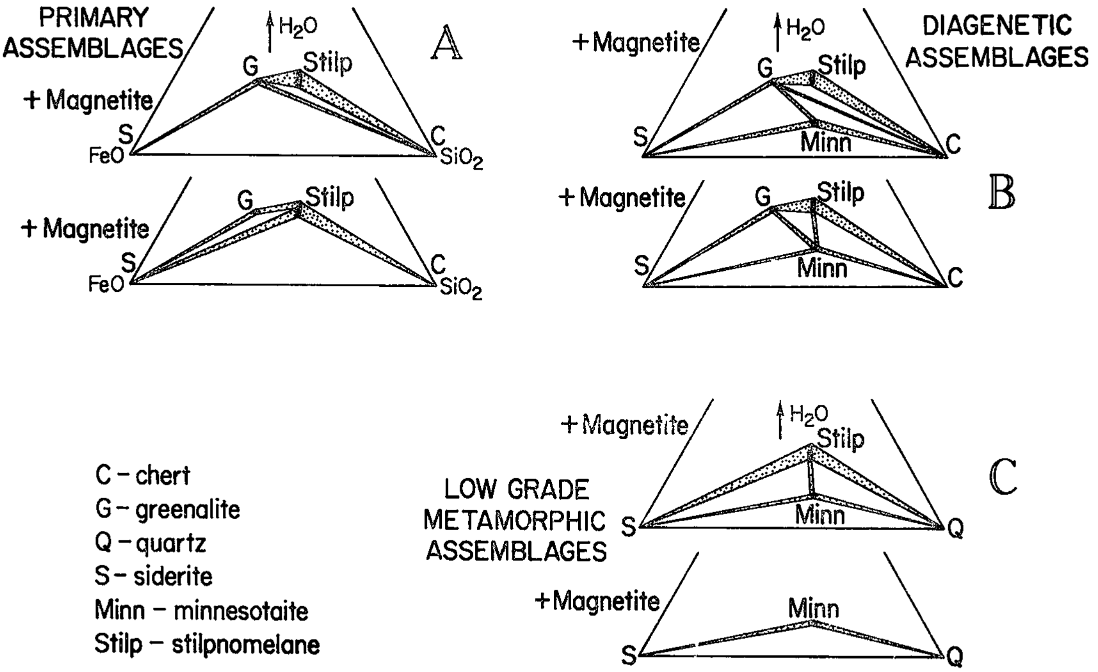

FIG. 12. Graphical representation of iron-formation assemblages in terms of FeO, SiO_2 and H_2O. For this representation all Fe in the Fe-silicates is assumed to be FeO only. CO_2 is considered as a perfectly mobile component. A. Primary assemblages of hydrous Fe-silicate gels, SiO_2 gel, magnetite-type precipitates and very fine-grained carbonate (siderite in the diagrams). B. Diagenetic assemblages resulting from the recrystallization of the original gels and fine-grained precipitates, and the onset of some minnesotaite formation. C. Low-grade metamorphic assemblages showing the disappearance of greenalite and stilpnomelane with the production of minnesotaite.

assemblage representations is shown in Figure 13 in which Fe^{2+} as well as Fe^{3+} are considered as components. The sequence of diagrams reflects the continuous change from primary to very low-grade metamorphic conditions. The complex reactions which are portrayed in this figure involve chert and siderite to form minnesotaite, the reaction of chert and greenalite (+ some Na, K, Al) to form stilpnomelane and the disappearance of greenalite and stilpnomelane to form minnesotaite. Textural evidence for many of the reactions has been presented above.

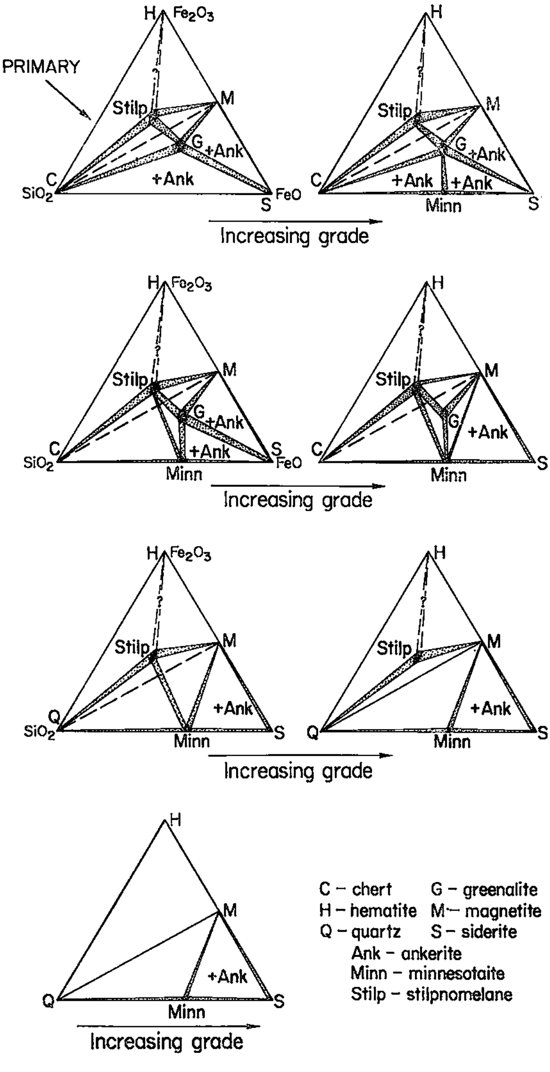

FIG. 13. Graphical representation of changes in iron-formation assemblages in terms of FeO, Fe_2O_3 and SiO_2. H_2O and CO_2 are considered as perfectly mobile components. This sequence of diagrams portrays the possible reactions which occur in changing from primary to low-grade metamorphic conditions. Hematite was not found as an oxide in the assemblages of this study. Coexistences in the primary assemblages are very similar to data from the literature on several Precambrian iron-formations (Klein 1973).

TABLE 10. REACTIONS FOR MINNESOTAITE FORMATION AS SHOWN TEXTURALLY IN FIGURES 5D, 6D, AND 7A TO 7D

$Fe_6Si_4O_{10}(OH)_8 + 4SiO_2$ *greenalite*	$= 2Fe_3Si_4O_{10}(OH)_2 + 2H_2O$ *minnesotaite*
$2Fe_6Si_4O_{10}(OH)_8 + O_2$ *greenalite*	$= 2Fe_3Si_4O_{10}(OH)_2 + 2Fe_3O_4 + 3H_2O$ *minnesotaite magnetite*
$3FeCO_3 + 4SiO_2 + H_2O$ *siderite chert*	$= Fe_3Si_4O_{10}(OH)_2 + 3CO_2$ *minnesotaite*
$..Fe_{2.7}Si_4(O,OH)_{12} \cdot xH_2O + 0.33Fe^{2+}$ *stilpnomelane*	$= Fe_3Si_4O_{10}(OH)_2 + H_2O + \overset{\text{minor}}{(Na^+, K^+, Ca^{++})}$ *minnesotaite*

The author concludes that all of the phases presently observed in the assemblages have sedimentary precursors in terms of gels, precipitates or oozes (see Table 10). During diagenesis, reorganization and recrystallization of these materials began, concurrent with diffusion of cation components to crystal structures which would provide a good fit. For example, Na and K cannot be housed in greenalite but can be incorporated in the more open stilpnomelane structure. Similarly, the disordered carbonate oozes began separation of $FeCO_3$-, $CaCO_3$- and $CaFe(CO_3)_2$-regions by means of diffusion of the various cations (equivalent to exsolution). Diffusion probably took place over short distances as there is no textural evidence for large distance remobilization of materials. Sporadic, fine fracture zones and chert fracture fillings in some granules are generally no longer than 1 mm. There is no evidence, therefore, for replacement textures in the sense of later solutions having dissolved and replaced earlier materials. The marked differences in grain size of some of the phases has often been considered as evidence for replacement processes. The extremely fine grain size of greenalite and therefore its lack of recrystallization, is probably controlled by misfits and mismatches in its crystal structure, as described earlier. The euhedral form and coarse grain size of magnetite, and the coarse grain size of ankerite, are concluded to reflect the strong force of recrystallization of these minerals in a very hydrous, low-temperature (diagenetic) environment.

There is much evidence in the assemblages, as presently observed, of approach to chemical equilibrium among the phases. Greenalite, although always extremely fine-grained, is homogeneous in composition. Similarly, coarser-grained stilpnomelane and minnesotaite show only very small ranges of composition. The carbonates show a very clear and consistent element fractionation pattern as shown in Figures 2 and 3. It is concluded, therefore, that the samples studied represent equilibrium assemblages of very low-grade metamorphic origin. Although specific temperature and pressure values cannot be obtained for such low-grade metamorphic iron-formation assemblages, French (1973) suggests a range of temperature of 150° to 350°C and a pressure range from 2 to 5 kb for such diagenetic to low-grade metamorphic conditions. Clearly, the assemblages represent conditions in the very low-temperature range of the greenschist facies.

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