SOME CHEMICAL CHARACTERISTICS OF THE PYROXENIC SKARNS FROM DOGNECEA, BANAT, RUMANIA

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Two pyroxene zones in skarns from Dognecea (Banat) contain Mn-ferrosalite and Mn-hedenbergite, respectively. These minerals are thermodynamically stable under pyrometasomatic conditions in environments rich in Fe^{2+}, Si, Ca, and O ($\pm$ Mg, Mn). During the hydrothermal stage the pyroxenes are replaced sometimes by ilvaite, and often by uralite, epidote, and (later) by carbonates and quartz.

The Zn, Pb, Cu deposits occurring in skarns at Dognecea have been known and mined since the sixteenth century. Early geological research mentions contact-metamorphic rocks in the region surrounding Dognecea (B.v. Cotta 1868, M. Castel 1869, H. Sjögren 1886, G. Halaváts 1889, 1890). In recent times, Ş. Vlad (1968 a, b) established some relationships concerning the zonality and the mineralogical composition of the skarn-bodies. Various research projects involving pyrometasomatic and hydrothermal assemblages emphasized the identification of approximately 60 minerals; Dognacskaite was described for the first time at Dognecea by J. S. Krenner (1884).

Metasedimentary rocks, represented mainly by paragneisses, Cretaceous iron deficient carbonate rocks of the Ezeriş-Cîrnecea syncline, and Laramian magmatites (banatites), predominantly granodiorites, occur in the Dognecea region (Fig. 1). Various thermal metamorphic and pyrometasomatic assemblages are found in the contact aureole of the banatitic body [illegible]a-Ocna de Fier-Dognecea. Carbonate rocks became highly crystalline marbles and, subsequently, were partly converted to skarns.

Garnetiferous skarns prevail close to the banatitic body, while further away pyroxenic skarns predominate, suggesting a periplutonic zonality inside the contact aureole (Ş. Vlad, 1968 a).

The main skarn-mass occurs on the west-limb of the Ezeriş-Cîrnecea syncline, between the Small Lake Valley (Valea Lacului Mic) and the Johann Valley (Valea Enăşoanei), displaying an assymmetrical disposition towards the contact of paragneisses with the carbonate rocks. Non-carbonate metasedimentary rocks have been in part replaced during the pyrometasomatical stage, sporadically forming grossularite-bearing lenses, while the carbonate rocks reacted

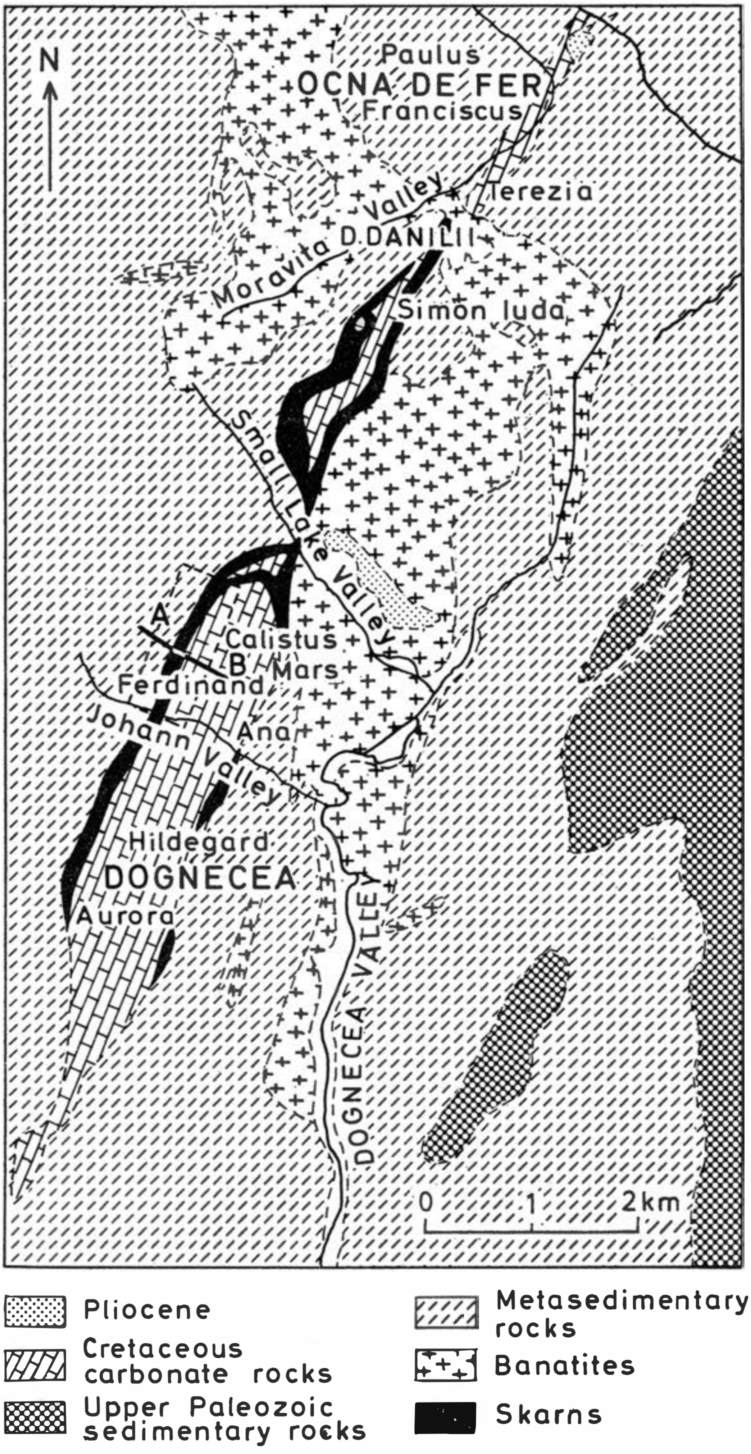

Fig. 1. Map of Ocna de Fer-Dognecea region, Banat, Rumania, showing simplified geological relationships (From: G. Halaváts 1888, 1890, and Al. Codarcea 1931).

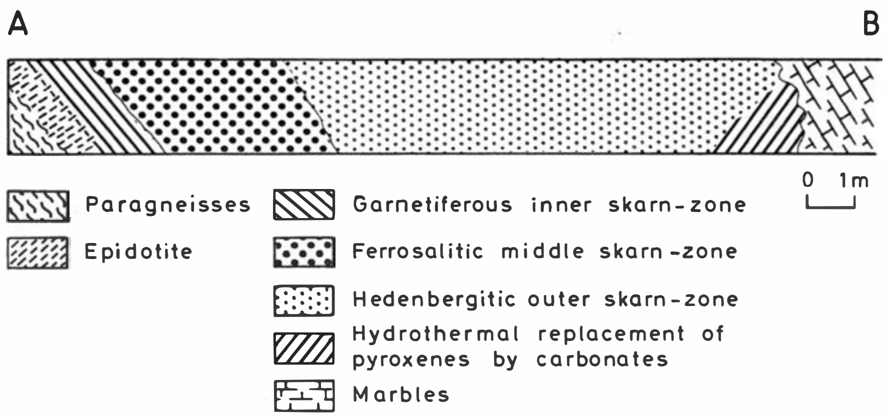

Fig. 2. Cross-section through the west-limb of the Ezeriş-Cîrnecea syncline showing skarn relationships (Vlad 1968a).

intensively with fluids, resulting in garnetiferous, pyroxenic and wollastonitic skarns (Ş. Vlad, 1968 a). The banded skarns, disposed parallel with the contact between paragneisses and carbonate rocks, may be subdivided into three zones (Fig. 2):

(1) Iron oxides-bearing inner zone, with andradite (1-2 m thick).

(2) Pyrite-bearing middle zone, with salite-ferrosalite$\pm$andradite (1-10 m thick).

(3) Sphalerite, galena, chalcopyrite-bearing outer zone, with hedenbergite$\pm$ andradite (5-15 m thick).

Mineralogic varieties of the Dognecea skarn pyroxenes are accurately defined by chemical analysis and reflect the mobility of different ions in the carbonate rocks during pyrometasomatical processes. It is well known that diopside-salite-ferrosalite-hedenbergite minerals form a complete solid solution series between $CaMgSi_2O_6$ and $CaFe^{2+}Si_2O_6$. Most of the minerals of this series, however, contain other ions, especially Mn. Usually the manganese content of the Mg-rich members is low, but the amount increases in the more Fe^{2+}-rich minerals (Deer, Howie & Zussman 1963). The replacement of Mg and Fe^{2+} by Mn is much greater in some skarn-pyroxenes than others, and it is most probable that diopside, hedenbergite, and johannsenite form a complete isomorphous group (Zharikov & Vlasova 1955).

PRESENT INVESTIGATION

One sample from the middle skarn-zone, and two samples from the outer skarn-zone were chemically analyzed, after previous selection and purification under a binocular microscope (Table 1). The analyses show manganoan varieties of ferrosalitic and hedenbergitic pyroxenes. The SiO_2 and CaO content are rather similar, showing a meagre decrease from the ferrosalitic member towards the hedenbergitic one (46.90 % to 45.41 % SiO_2 and 23.41 % to 21.03 % CaO) while, on the other hand, variations in the Fe^{2+}, Mg and Mn contents

Table 1. Diopside-hedenbergite-johannsenite chemical analyses

1. Manganoan ferrosalite, middle skarn-zone, Dognecea (Banat)
2. Manganoan hedenbergite, outer skarn-zone, Dognecea (Banat)
3. Manganoan hedenbergite, outer skarn-zone, Dognecea (Banat)

	1	2	3
SiO_2	46.90	46.21	45.41
TiO_2	0.19	0.06	0.05
Al_2O_3	2.17	1.21	1.21
Fe_2O_3	2.40	3.82	1.67
FeO	11.58	15.18	12.63
$Fe(FeS_2)$	0.09	–	–
MnO	3.76	8.39	11.47
MgO	6.14	1.92	2.03
CaO	23.41	21.03	22.64
H_2O	0.96	0.96	0.68
CO_2	1.61	0.46	0.96
$S(FeS_2)$	0.10	–	–
Total	99.31	99.24	98.75

Numbers of ions on the basis of 6 oxygens

	1		2		3	
Si	1.963	2.00 (Si, Al)	1.930	2.00 (Si–Ti)	1.928	2.00 (Si–Ti)
Al	0.064		0.060		0.061	
Al	0.041	1.975 (Al–Ca)	–		–	
Ti	0.007		0.001		0.001	
Fe^{3+}	0.074		0.121	1.975 (Fe^{3+}–Ca)	0.052	2.00 (Fe^{3+}–Ca)
Fe^{2+}	0.399		0.531		0.447	
Mn	0.132		0.296		0.412	
Mg	0.377		0.119		0.129	
Ca	0.944		0.917		0.974	

are significant. The sample from the middle skarn-zone contains 6.14% MgO and 3.76% Mn, and on this basis should be considered *manganoan ferrosalite*. The two pyroxene samples from the outer skarn-zone have a small content of MgO (2.03% and 1.92% respectively), but a greater MnO content (11.47% and 8.39% respectively), establishing them as the variety *manganoan hedenbergite*. (C. O. Hutton, 1956, has suggested that the distinction between johannsenite and hedenbergite should be made on the basis of the dominant molecule present. Minerals having a composition closer to johannsenite than hedenbergite are described as ferroan johannsenite, and those closer to hedenbergite as manganoan hedenbergite.) The molecular proportions of the end-members of each pyroxene confirm the identification (Table 2).

The genesis of apocarbonate pyroxenic skarn requires a remarkable supply of Si and Fe^{2+}, showing a progressive increase of Fe^{2+} content towards the outer zone (from 11.48% to 15.18%). Mg^{2+} had a limited mobility, with

Table 2. The molecular proportions of the end-members

1. Manganoan ferrosalite, middle skarn-zone, Dognecea (Banat)
2. Manganoan hedenbergite, outer skarn-zone, Dognecea (Banat)
3. Manganoan hedenbergite, outer skarn-zone, Dognecea (Banat)

	1	2	3
Diopside	40	13	12
Hedenbergite	43	56	45
Johannsenite	17	31	43

Mg^{2+} concentration decreasing in the direction of infiltration of metasomatic fluids (from 3.76% to 11.47%).

Subsequently, skarn-minerals experienced a retrogressive metamorphism resulting in alteration of the pyroxenes. The reaction between hydrothermal iron-bearing fluids and manganoan hedenbergite produced ilvaite. The chemical analysis of ilvaite (Table 3) indicates an introduction of Fe^{2+} and Fe^{3+}, while its MnO content is similar to that of manganoan hedenbergite, thus establishing it as the variety *manganoan ilvaite.*

The progressive decrease of the temperature and iron concentration caused changes in character of the hydrothermal solutions. As a result the pyroxenes were replaced by uralite, epidote, and, later, by the assemblage dolomite+calcite+quartz.

Table 3. Ilvaite chemical analysis

Manganoan ilvaite, outer skarn-zone, Dognecea (Banat)		Numbers of ions on the basis of 9(O, OH)		
SiO_2	28.89	Si	1.94	2
TiO_2	0.04	Al	0.06	
Al_2O_3	2.31	Al	0.12	1.14
Fe_2O_3	20.18	Fe^{3+}	1.02	
FeO	24.32	Fe^{2+}	1.36	1.88
MnO	8.30	Mn	0.47	
MgO	0.54	Mg	0.05	
CaO	13.74	Ca	0.98	
H_2O	2.07	OH	0.93	
Total	100.35			

SUMMARY

Thermo-metamorphic, pyrometasomatic, and hydrothermal assemblages of various kinds occur in the contact aureole generated by the Laramian magmatites in the Dognecea region. Apocarbonate zoned skarns exposed near the contact between carbonate rocks belonging to Ezeriş-Cîrnecea syncline and paragneisic rocks are composed of garnets, pyroxenes, and wollastonite.

Pyroxene varieties (manganoan ferrosalite and manganoan hedenbergite) form the main bulk of these skarns, represented by members of the diopside-hedenbergite-johannsenite series.

The genesis of pyroxenic skarns involved a supply of Fe^{2+} and Si to all zones, some Mg closer to the contact between paragneisses and carbonate rocks, and Mn, especially in the outer zone. During the hydrothermal stage the pyroxenes have been altered, sometimes replaced by ilvaite, often by uralite, epidote, and, later, by the dolomite+calcite+quartz assemblage.

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