

An occurrence of ilvaite layers in the Cinco Villas metasomatic rocks, Western Pyrenees (Spain)

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ABSTRACT. In the Artikutza area, near the contact with the southern Aya granite, skarns containing hedenbergite, grandite, epidote, quartz, calcite, actinolite, idocrase and magnetite occur and have been found to contain ilvaite layers. This is the second reported occurrence of ilvaite in Spain; spectral reflectances, colour values, Vickers hardness numbers and chemical composition are given. The monomineralic ilvaite lens intercalation developed by hydrothermal alteration of hedenbergite in a second stage of skarn formation.

KEYWORDS: ilvaite, skarns, reflectivity, Aya granite, Spain.

EARLIER papers have referred to the occurrence of ilvaite in metamorphosed iron deposits (Machairas and Blais, 1966), Ca-Fe-Si skarns (Bartholomé and Dimanche, 1967; Burt, 1971; Verkaeren, 1974; Plimer and Ashley, 1978) and as a late-stage alteration product in some basic rocks (Naslung *et al.*, 1983; Barton and Bergen, 1984). The first occurrence of ilvaite in Spain was reported from the Burguillos del Cerro skarn southwest of Badajoz as containing magnetite and vonsenite (Ruiz, 1976). There it occurs as rare and irregular grains up to 0.05 mm in veins crossing magnetite.

Cell parameters of ilvaite, $\text{CaFe}_2^+\text{Fe}^{3+}\text{Si}_2\text{O}_8(\text{OH})$, obtained from refined X-ray powder diffraction data are $a = 8.82$, $b = 13.07$, and $c = 5.89 \text{ \AA}$. The systematic absences give a *Pbnm* space group (Belov and Mokeeva, 1954; Beran and Bittner, 1974).

A reflected light investigation of ilvaite from Rio Marina, Elba, Italy, was performed by Beran (1980). He measured the spectral reflectances of crystal faces parallel to (100) and (001) and determined that the signs of the birefringence and absorption of the mineral were negative.

In this paper we discuss the mode of occurrence, mineral assemblage, chemical composition, optical behaviour and Vickers hardness variation of the ilvaite from the Cinco Villas Palaeozoic massif in the western Pyrenees.

Occurrence of ilvaite

Macroscopic appearance. The ilvaite is located in the Artikutza area, about 15 km southeast of San Sebastian, Spain, near the southern contact with the Aya granitic massif (fig. 1). The full extent of this skarn is not known as exposures are poor. Near the granite contact, hornfels rocks of pelitic composition containing porphyroblasts of andalusite and rare Ca-Fe-Si skarn intercalations appear to be concordant within a sequence of predominantly clastic metasedimentary rocks of Westphalian age (Campos, 1979). Carbonate beds are known in the Carboniferous system of Cinco Villas. They typically consist of recrystallized calcite with minor disseminated pyrite and a clastic fraction. Locally there are associated hematite and magnetite ore deposits.

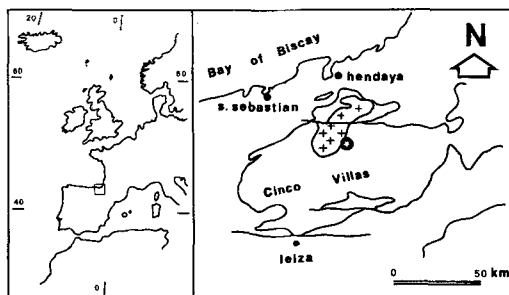


FIG. 1. Simplified geological map of western Pyrenees showing the position of the Aya granite in the Cinco Villas massif and the setting of the ilvaite area (Artikutza).

Ilvaite appears as black bands usually less than 50 mm thick, associated with hedenbergite and epidote bands. Surrounding calcareous shales, extensively metasomatized at the contacts with the

skarns, contain predominantly green amphibole, garnet (grandite), idocrase, calcite, quartz, fluorite, etc., but these are not associated with marbles.

Hedenbergite bands are nearly monomineralic with bladed crystals up to 70 mm long in radiating aggregates. Ilvaite bands of coarse grained crystals up to 8 mm long, occurs at the more Fe-rich horizons.

Microscopic appearance. In thin section the ilvaite from the intercalated lenses is granoblastic in texture; individual crystals are subidioblastic, usually prismatic, and are randomly oriented with respect to the lens surfaces. The grain size is generally less than 5 mm. Ilvaite is nearly opaque in this section due to its strong absorption; its red colour is due to preferential absorption in the blue and ultra-violet region of the spectrum.

Physical properties

Ilvaite occurs as prismatic crystals developed in the direction of the *b*-axis and as massive inter-grown aggregates. We have identified the prism $\{h0l\}$ and basal pinacoid $\{0k0\}$. The complex aggregates do not permit a complete morphological study.

In polished section, ilvaite displays very distinct reflectance pleochroism from dull grey with a bluish tint to brownish yellow grey (the latter on sections cut at right angles to the elongation of the prism). The anisotropy is very strong with orange-red colours.

The mineral polishes well, being harder than the neighbouring silicates. In general, a series of 10 indentations was performed with each load. Indentations showed slightly fractured shapes. Mean and standard deviations of all diagonals measured were computed. The Vickers hardness average value of ilvaite was 613 Kp/mm² if square loads are plotted as a function of the diagonal. This value is lower than those obtained with loads of 100, 200, and 400 p (645 ± 57, 655 ± 43 and 640 ± 44, values of Vickers hardness respectively).

Quantitative reflectance measurements were made at 20 nm intervals throughout the visible spectrum using a MPV-Leitz microphotometer equipped with a continuous line interference filter. A Zeiss SiC (No. 125) reflectance standard and × 16 and × 25 oil objectives was used for all measurements. An immersion oil conforming with the requirements of the COM was used ($n_D^{23} = 1.515$, $v = 49$, DIN 58.884). Statistical and systematic errors have been taken into account (Piller, 1977). The air and oil reflectance curves (fig. 2, Table I) show a greater difference in values at the upper end of the visible region (560–700 nm). Values of the refractive indices calculated with Fresnel's formula

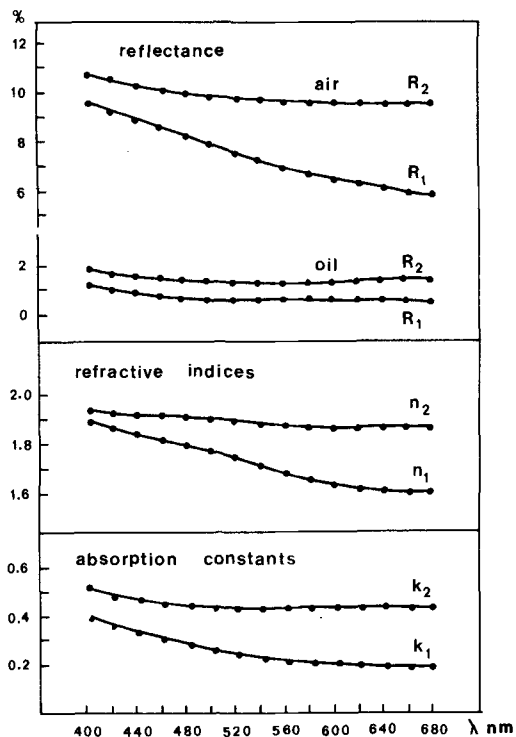


FIG. 2. Dispersion curves for the maximum and minimum (2) reflectance (*R*), refractive index (*n*) and absorption constants (*k*) of ilvaite, in air and oil ($n_D = 1.515$).

are shown in Table II; they are very similar to those obtained by Beran (1980).

Quantitative colour values have been established by the weighted-ordinate method (Atkin and Harvey, 1979) (Table I), and calculated for a C-source ($x = 0.3101$ and $y = 0.3162$). If *x*-*y* coordinates are plotted, a chromaticity just to the blue side of the illuminant C is determined. In air and oil the combination of lower luminance and higher excitation purity (very high in oil) explains the characteristic blue-grey colour.

Chemical composition

The chemical composition of ilvaite determined with microprobe analyses showed a particularly Fe-rich character. The average composition from microprobe analyses of three representative points (Table III) corresponds to different ilvaite crystals in the same band. Chemical analyses were performed for FeO and Fe₂O₃ in separated and purified ilvaites. The structural formula was established assuming that the cation sum is 6 on the basis of 8.5 oxygens. This composition is close to the ideal

TABLE I. Spectral reflectivity values (R) for ilvaite in air and oil

λ(nm)	Air		Oil	
	R ₁	R ₂	R ₁	R ₂
400	9.50	10.60	1.10	1.80
420	9.00	10.25	1.00	1.60
440	8.75	10.10	0.85	1.50
460	8.50	9.90	0.80	1.40
480	8.20	9.85	0.75	1.35
500	7.80	9.77	0.70	1.35
520	7.50	9.70	0.60	1.35
540	7.30	9.60	0.55	1.35
560	6.80	9.55	0.50	1.35
580	6.50	9.50	0.45	1.35
600	6.25	9.50	0.45	1.35
620	6.00	9.50	0.45	1.35
640	5.85	9.50	0.40	1.40
660	5.75	9.50	0.40	1.45
680	5.75	9.45	0.40	1.45
700	5.70	9.40	0.40	1.45

x	0.3059	0.2823	0.3064	0.2594
y	0.3113	0.2924	0.3067	0.2610
Y%	9.59	6.93	1.35	0.2610
P.e(%)	2.10	12.76	3.17	24.87
λ _D	473.9	479.7	-565.7	476.0

x, y --- chromaticity coordinates. Y --- luminance.
P.e --- excitation purity. λ_D --- dominant wavelength.

ilvaite. Only small amounts of Al³⁺, presumably replacing Fe³⁺ and Si⁴⁺, and a little Mn²⁺ and Mg²⁺ replacing Ca²⁺ and Fe²⁺ occur. These deviations from the ideal composition are typical of ilvaites from skarn deposits (Leonard *et al.*, 1962; Plimer and Ashley, 1978). In the same way, the low MnO contents reported in the microprobe analyses (about 1.30 wt. %) are in agreement with the increasing d₀₂₀ peak in the X-ray powder data (Plimer and Ashley, 1978), and they show good agreement with the Mn-contents of ilvaites from Fe-rich calc-silicate rocks.

Discussion

The ilvaite-bearing assemblages of the Artikutza area mostly consist of monomineralic hedenbergite with monomineralic ilvaite lenses. Fe-rich sedimentary carbonates with iron deposits (hematite and magnetite), located in this Palaeozoic massif may be transformed into hedenbergite or into hedenbergite magnetite in the neighbourhood of the intrusion. The ilvaite has its origin in later metasomatism of the hedenbergite assemblages formed in the first stage of the skarn formation. The second

TABLE II. Optical parameters of ilvaite

λ(nm)	n ₁	k ₁	κ ₁	n ₂	k ₂	κ ₂
400	1.93	0.52	0.27	1.90	0.40	0.21
420	1.92	0.49	0.25	1.86	0.37	0.20
440	1.92	0.47	0.25	1.85	0.34	0.19
460	1.91	0.45	0.24	1.83	0.33	0.18
480	1.91	0.45	0.23	1.80	0.31	0.17
500	1.90	0.44	0.23	1.76	0.30	0.17
520	1.89	0.44	0.23	1.74	0.27	0.16
540	1.88	0.44	0.23	1.73	0.26	0.15
560	1.87	0.44	0.23	1.68	0.24	0.14
580	1.87	0.44	0.23	1.66	0.22	0.13
600	1.87	0.44	0.23	1.64	0.22	0.13
620	1.87	0.44	0.23	1.61	0.22	0.13
640	1.86	0.44	0.24	1.61	0.20	0.13
660	1.86	0.45	0.24	1.56	0.20	0.13
680	1.85	0.45	0.24	1.60	0.20	0.13
700	1.84	0.45	0.24	1.59	0.20	0.13

λ wavelength
n refractive index
k absorption coefficient
κ absorption index

hydrothermal stage, presumably introduced along bedding planes, produces alteration of hedenbergite and other metamorphic minerals into ilvaite; stylolites and bedding are nearly parallel to the black layers of the hedenbergite-ilvaite rocks.

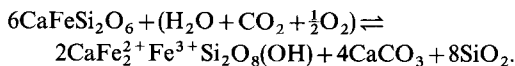
The rarity of monomineralic ilvaite layers must

TABLE III. Chemical composition of ilvaite from Artikutza

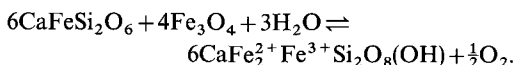
	wt% (*)	Number of ions on the basis of 9.5 oxygens.	
SiO ₂	29.90	Si	2.018
TiO ₂	0.10	Ti	0.005
Al ₂ O ₃	1.00	Al	0.079
Fe ₂ O ₃	17.76	Fe ³⁺	0.903
FeO	31.90	Fe ²⁺	1.801
MnO	1.30	Mn	0.074
MgO	0.27	Mg	0.050
CaO	14.00	Ca	1.048
K ₂ O	0.05	K	0.004
Total	96.28		5.982 = 6.00

(*) Mean of three analyses.
Analyst: F. Autefage. Univ. Paul Sabatier (Toulouse, France).

be explained by a very restricted range of stability conditions and original composition of the altered rocks: i.e. decreasing temperatures, high $\mu_{\text{H}_2\text{O}}$ and very low μ_{CO_2} , and probably fairly high to medium oxygen fugacities (Bartholomé and Dimanche, 1967; Verkaeren and Bartholomé, 1979). The stability fields of ilvaite imply the action of a fluid phase with exceedingly low X_{CO_2} , first on hedenbergite or, later, on hedenbergite-magnetite assemblages. The following equilibrium must explain the ilvaite formation by hydrothermal alteration:



If an earlier-formed magnetite-bearing hedenbergite assemblage is altered during the hydrothermal stage, a nearly monomineralic layer may be separated:



These hydrothermal assemblages are as a rule more complex and are never monomineralic, but the ilvaite-bearing rocks studied have rarely minor amounts of calcite (Verkaeren and Bartholomé, 1979).

The hydrothermal stages in this metasomatic replacement of hedenbergite takes place at about 450 °C under low pressure. Ilvaite is stable only at temperatures below 470 °C if the pressure is about 2 kbar (Burt, 1971; Gustafson, 1974).

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[Manuscript received 31 January 1985;
revised 17 February 1986]