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CHARACTERIZATION OF KALIMASHI CHROMITE ORE (ALBANIA) BY SCANNING ELECTRON MICROSCOPY

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Abstract

The textural and structural characteristics of chrome ores mined in Albania have been examined by means of scanning electron microscopy (SEM) analysis. Elemental mapping and microanalysis of Cr, Fe and Al (to identify the chromite phase) and of Mg and Si (to identify the olivine) have been carried out. A study has been made of the kind of micro-inclusions found in the ore, in order to evaluate the products of the beneficiation processes.

Textural complexity of the ore explains the difficulties involved in obtaining good recoveries and high-quality concentrates.

Key Words: Scanning Electron Microscopy, Chromite Ore, Texture, Structure, Beneficiation.

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Introduction

Mining and processing of chromite play a very important role in the economy of Albania, which is one of the world's major producers of chrome ores. Exploration carried out in recent years has led to the discovery of many new ore bodies, including a large one at Bulquiza, which lies in ultrabasic massif northeast of Tirana. The massifs of Batra and Thekna are formed of the same ultrabasics (Ramdohr, 1980). Other ore bodies occur in the more northerly massifs of Tropoja (Kam, Ragam) and Kukes (Kalimashi) (Pumo, 1977). Until a few years ago the extraction of chrome ore presented no particular difficulties, because of the shallow depth of the mines and the high chromium grades encountered. The situation has now changed considerably: depths are greater and the ores are leaner. Beneficiation is thus essential to make mining an economic proposition.

Deeper-seated ores have different textural and structural characteristics and their relationship with the gangue is also more complicated. The change from nodular or massive textures in the shallow-seated ores to the generally highly diffused textures of the deeper-seated ones requires finer grinding which generates larger quantities of fines and causes beneficiation difficulties and reduction in chromium recovery. In this context it is important to examine the following parameters:

1. Textural and structural characteristics of the ore and relations between chromium minerals and gangue, as well as the amount of serpentinization and their influence on the beneficiation process.
2. Particle shape and analysis (to assess their influence on classification processes).
3. Degree of liberation of ore (to obtain useful data on comminution in relation to energy consumption and the production of fines).

Kalimashi Chromium Deposit

The ore examined is obtained from the Kalimashi deposit in the ultrabasic massif of Kukes which consists mainly of dunites and harzburgites, plus other ultrabasics and basics of limited extent (Cina et al., 1986). The tectonic sequence has a measured thickness of 1000 to 2000 m, whereas the cumulate sequences are 600 to 1500 m thick (Goci et al., 1981). Cumulate dunites are thicker in the latter, while other sequences (ultrabasics and basics) are thinner and tend to occur only in certain areas (Dede, 1965). The Kalimashi deposit is found within massive ultrabasic formations of volcanic-sedimentary origin. There are three zones in the chrome-ore occurrence each with different petrographic and structural characteristics. The transitions from one formation to another are gradual and often difficult to identify (Cina, 1970).

The process that originated the various mineralizations is linked to magmatic segregation phenomena. This process produced areas with different contents and diverse concentrations of magma elements. The primary mineralogical association consists of chromite-iron-spinel and olivine. Subsequently pyroxenes were formed; these occur as veins throughout the formation (Caslli and Cina, 1982). Serpentine, formed by serpentinization of olivine and pyroxene, and auto-metamorphism, is present. Secondary minerals also include magnetite, chlorite (clinochlore), sulphides (pentlandite and chalcopyrite) and hydrothermal calcite.

The tectonic ultrabasics are high in olivine, of approximate composition 92% Mg_2SiO_4 - 8% Fe_2SiO_4 to 95% Mg_2SiO_4 - 5% Fe_2SiO_4 and contain a limited amount of orthopyroxene of the approximate composition 92% $MgSiO_3$ - 8% $FeSiO_3$ to 92% $MgSiO_3$ - 8 % $FeSiO_3$, but clinopyroxene $Ca(Mg,Fe,Al)(Si,Al)_2O_6$ is very rare. The rocks are also high in magnesia, very low in Al_2O_3, CaO, Na_2O, K_2O and TiO_2, and relatively high in NiO (Serjani and Tophana, 1970). Chromite ore bodies occur throughout the sequences starting from the tectonic harzburgites in the deepest known part of the section and running to the troctolite gabroolivinites at the top. However the major concentration of chromite deposits is associated with the tectonic harzburgite sequence containing dunite intercalations and to a lesser extent, with the cumulate dunites (Shallo et al., 1981).

In the deepest tectonic harzburgite sequence, the chromite is of the Al-rich type, and the deposits are podiform. Those parts of the sequence containing intercalations of dunites, averaging 5 to 20 m in thickness, include a number of very large podiform ore deposits and mineral occurrences, some of which are platy and strongly folded, while others are vein-like, or lens-form, dipping at very high angles. The structure of the ores is massive with dense to middling disseminations and partly nodular, whereas the texture is subheudral with 1 to 2 mm grains and sometimes euhedral (3 to 6 mm). The chromite is of the Cr-rich type (Cina, 1970).

The chromite ores in the tectonic harzburgite sequence have a higher FM [FM: $Fe^{2+}/(Fe^{2+} + Mg)$] ratio than those in the harzburgite-dunite tectonites, while in the cumulate sequences with dunite, pyroxenite, ultrabasics and basics, the ratio increases. A systematic variation of Cr^* [Cr^*: Cr / (Cr + Al + Fe^{3+})] is observed, being low in the chromites of the deepest tectonic harzburgite sequence and very high in the harzburgite-dunite tectonites and cumulate dunites; it is also low in the ultrabasic-basic and basic cumulate sequences. The Cr^* and FM values indicate that the harzburgite-dunite tectonites of all the massifs are similar. These features of the chromites and the geological setting of the ore deposits indicate that they were formed in various ways during perturbed conditions (Gjokuta, 1980).

The Al-rich chromites of the deepest sequence were formed by crystallization of an ore melt accumulated as a consequence of very limited melting of the upper mantle. On the contrary, the Cr-rich chromites of the tectonic harzburgites with thin dunite intercalations were formed by the crystallization of an ore melt accumulated as a consequence of a more marked partial melting of the upper mantle and were subjected to intensive deformations during crystallization. The chromites of the cumulate sequences, instead, were formed by fractional crystallization of the melt in the upper part of the mantle (Ndojaj, 1988).

In addition to these processes, cementation of ore clasts by silicates is also to be observed, as is metasomatosis of the chromite due to pneumatogene-hydrothermal processes, which led to their relative enrichment in Al.

The composition, resulting from chemical analyses, of the Kalimashi ore is given in Table 1. The analytical procedure adopted to quantitatively determine the different mineral species present in the ore was as follow:

a) A certain number of samples of the main mineralogical phases (chromite, olivine, serpentine) constituting the ore were selected by densimetric analyses and optical microscope control.

b) Each selected sample ("pure" minerals was analyzed chemically to determine the elementary composition.

c) Quantitative diffractometric and chemical analyses were then carried out on the ore.

Starting from the results obtained by the different analyses and from the comparison of the different sets of data ("pure" minerals and ore composition) the results presented in Table 1 were derived.

Table 1: Chemical composition (% content as oxides) of the Kalimashi chromium ore and the main constituent minerals.

Composition of constituent minerals

Oxides	Crude ore	Chromite	Olivine	Serpentine
SiO_2	18.64	1.85	40.80	33.80
Cr_2O_3	30.22	58.82	0.38	1.80
Al_2O_3	5.96	11.12	1.45	0.99
Fe_2O_3	1.79	2.75	-	3.98
FeO	9.60	13.10	5.10	1.79
MgO	27.87	12.30	50.00	40.00
MnO	0.13	0.18	0.07	0.07
CaO	0.14	0.30	1.05	1.40
NiO	0.18	0.07	0.34	0.27

Chromite	:	$(Mg,Fe)Cr_2O_4$
Olivine	:	$(Mg,Fe)SiO_4$
Serpentine	:	$Mg_6(Si_4O_{10})(OH)_8$

Ore Samples

The ore samples were obtained from run-of-mine lumps. Samples of comminution products were also examined. All the samples were mounted in resin and then installed in an aluminium sample-holder 1 inch (2.5 cm) in diameter. All the resin-mounting processes were carried out a temperature of approximately 70°C, in order to attain proper fluidity and a better coating of the material. Particular care was taken during polishing the samples in order to minimize disturbance of surface characteristics (fractures and discontinuities). All the samples were machine polished using finer and finer emery paper, after which they were hand polished using a series of diamond pastes starting from 3 micrometers and finishing at 1 micrometer. All the samples were coated with gold by vacuum evaporation.

Methods of Investigation

Optical Microscope Observation

A Zeiss Neophot II microscope was employed for optical investigation using reflected light and a Zeiss WC polarizing microscope for transmitted light, while the lump ore was studied by means of a Reichert binocular microscope. The purpose of these preliminary observations was to acquire data to facilitate scanning electron microscopy and electron microprobe analyses. The ultimate aim was to identify the various minerals present in the ore, and to ascertain their distribution and associations, as well as the most frequent types of contacts. These parameters were of great importance for the performance of the following investigations.

SEM and electron microprobe analysis

The analyses were performed using a Philips SEM 505 equipped with an EDAX 9900 microanalysis system. Both BEI (back-scattered electron image) and XRM (X-ray mapping) analyses were performed on each sample. This approach reveals the mutual relations among the various minerals, the existence of micro-inclusions and the type and magnitude of the intergrowths (Reed, 1975; Jones, 1974). Mapping of the elements Cr, Al and Fe was used to ascertain the presence of chromite, and mapping of Mg and Si to detect olivine (Gulson and Lovering, 1968). Ca mapping was also performed to check the presence of calcite of secondary origin.

Results and Discussion

Investigations of opaque and transparent minerals under an optical microscope showed that the main minerals are chromium-iron-spinel, olivine and serpentine. Accessory minerals are magnetite of secondary origin, amphiboles, chlorite and sulphides. The ore contains approximately 24% of chromium-iron-spinel, 50% of olivine and about 20% of serpentine.

SEM observations permit the characterization of various types of texture in the chrome ore, namely: a) massive texture characterized by generally homogeneous distribution of chromite particles (from the morphological and morphometric aspects) within the olivine matrix; b) disseminated texture characterized by chromium particles dispersed within the olivine matrix; c) linear texture characterized by grains of chromite, with an elongated shape and iso-orientation (the spacing of the lines along which iso-orientation occurs is variable and the lines themselves sometimes merge); and d) patch texture characterized by zones of rather irregular shape consisting only of chromite (Bonifazi et al., 1989).

The chromite is often associated with olivine and serpentine (gangue mineral). The chromite grains are irregular in shape with lined surfaces. The contact with gangue minerals is clear and regular. Metamorphism is low-grade, as is evident from the small quantity of secondary magnetite, which, when present, occurs as thin light-coloured veins. The chromite is generally fractured, the cracks often contain serpentine (chrysotile). More rarely, chlorite inclusions occur as micro-tabular and tabular aggregates in the chromite.

The olivine and dunite often exhibit fracture systems and are affected by a low grade of serpentinization. The olivine is mainly of the magnesia type. The serpentine, originated by serpentinization of olivine and pyroxenes, is of the chrysotile and antigorite types. It occurs as thin veins which form networks or fibrous aggregates. The metamorphism process of serpentine have produced secondary magnetite, and when the amount of oxygen is less, produce hematite, which in the alteration zone gives limonite. Chlorite, as well as, pentlandite and chalcopyrite are rarely present.

SEM analyses of the ore show the presence of chromite both in idiomorphic forms and as patches (Figs. 1, 2a and 2b). The gangue in most cases is olivine (Fig. 2c), which is often altered to serpentine at the boundary (Fig. 2d). The chromite (Fig. 2a) is frequently affected by systems of microfractures containing serpentine. SEM analyses were particularly useful in revealing the alteration area around the particles of olivine; optical microscopic analyses are very difficult in clearly establishing the characteristics of the alteration zone (width, profile, cracks and microinclusions as analyzed in Figs. 2c and 2d).

In some samples, chromite is found disseminated in an olivine matrix (Fig. 3). In this case, the chromite occurs as particles that may be regular or irregular in shape. The larger the particles the more irregular the shape. In this case also, both the chromite and olivine are affected by microfractures containing serpentine.

Gangue minerals include pyroxene, as shown in Fig. 4, at the contact with olivine. The passage between the two phases is always clear and the profile is irregular. Inclusions in the olivine contain magnetite in addition to chromite (Fig. 5). Magnetite is present both in finely dispersed form and as aggregates with irregular, highly-contorted boundaries.

SEM examination has, in particular, revealed especially important aspects regarding the structural characteristics of the chromite. Rarely are isomorphic crystals encountered (Fig. 4). More frequently the crystals are hypidomorphic and allotriomorphic owing to the different degrees of crystallization of various mineral phases and the magma, as well as the diverse concentration of elements within the latter.

The presence of alteration structures and substitution affecting the chromium grains points clearly to serpentinization caused by the remobilization of Cr, Al and Mg ions as a result of circulation of hydrothermal solutions (Figs 3 and 4).

The SEM studies carried out on diverse samples of various screen-size classes resulting from comminution show that the textural characteristics of the grains are similar to those found in the ore. Each sample was obtained following this procedure:

a) a certain amount of material coming from the ore was isolated and sampled for each of the different textures constituting the ore;

b) each sample was subjected to the same comminution process (see results in Table 2);

c) the degree of liberation of the different products (same size class but different textural

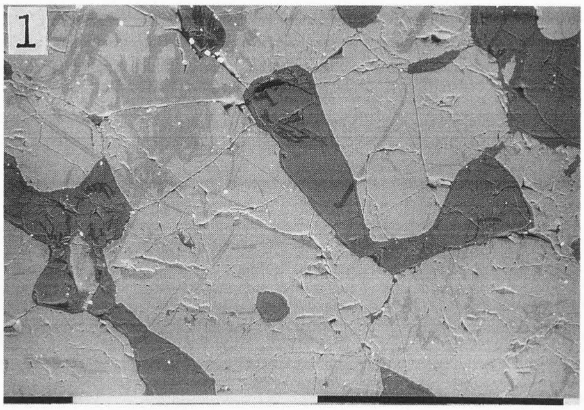
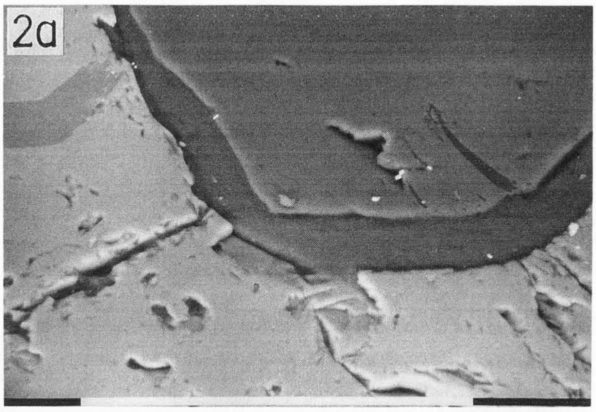
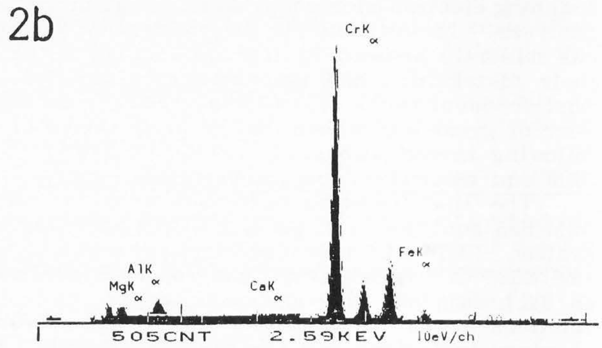
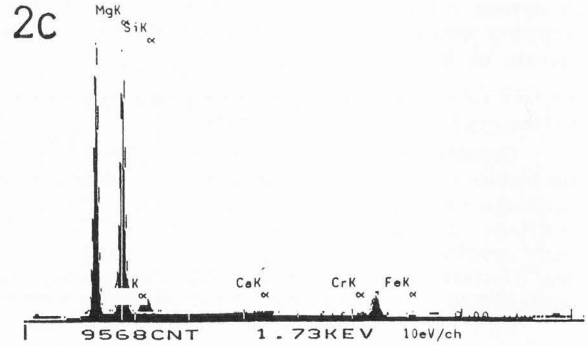


Figure 1. Kalimashi Chrome Ore, as mined back-scattered electronic image (BEI). The variability of textural characteristics is evident. Chromite is present both as patches of variable shapes and sizes and as idiomorphs. Fractures occur throughout the whole sample; these are filled with serpentine (chrysotile and microantigorite types). This situation is indicative of the tectonic movements that have affected the ore body. Length of white bar = 1 mm.







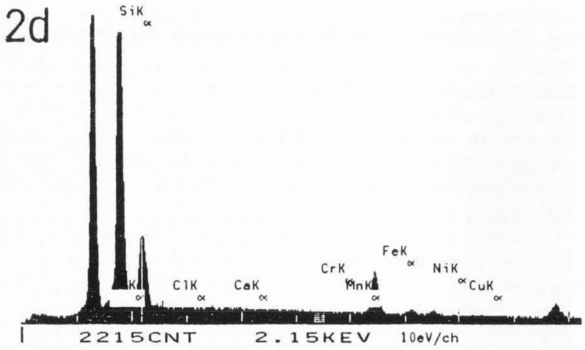


Figure 2a (at right). Kalimashi Chrome Ore, as mined (BEI). Details of the area of contact among olivine (medium grey), serpentine (dark grey) and chromite (light grey); the latter is affected by fractures and corrosion. Serpentine is in the discontinuities. The contact between gangue and chromite is regular. Note how the serpentine represents the olivine alteration process. Length of white bar = 0.1 mm. Microanalysis of various areas of the sample (see photograph, Fig. 2) reveals the composition of each phase: **Fig. 2b** - light grey - chromite; **Fig. 2c** - medium grey - olivine; and **Fig. 2d** - dark grey-serpentine.

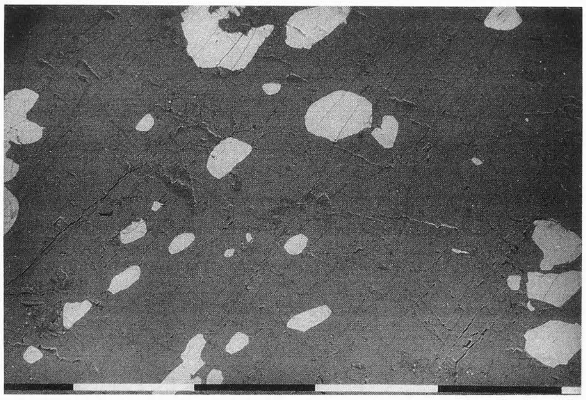
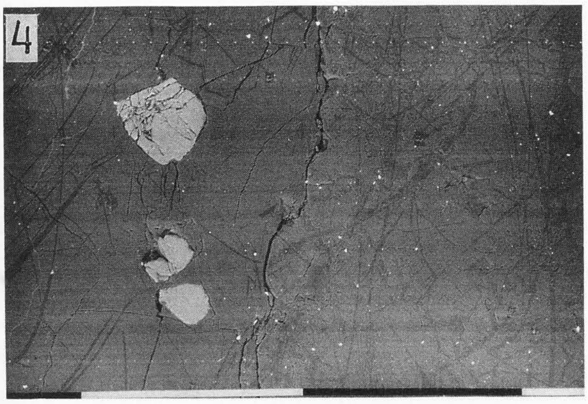


Figure 3. Kalimashi Chrome Ore, as mined (BEI). Chromite (light grey) is disseminated in the olivine (medium grey). Chromite is present as both, regular and irregular, particles. It is often affected by microfracture systems filled with serpentine. Length of white bar = 1 mm.



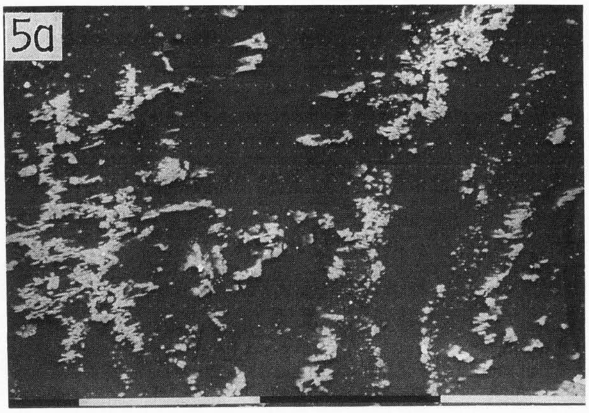
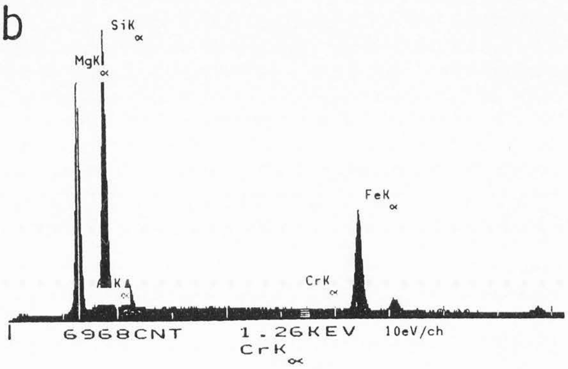


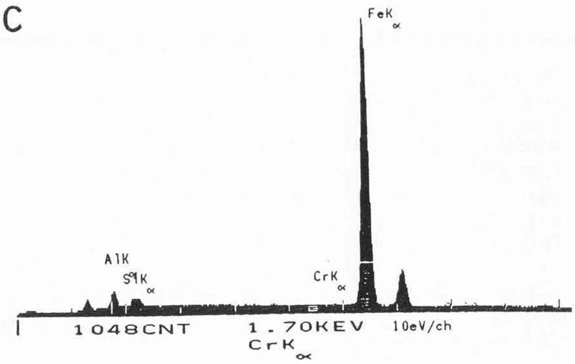
Figure 4. Kalimashi Chrome Ore, as mined (BEI). Three different minerals may be noted: chromite (light grey) and olivine (dark grey), both on the left of the photo, and pyroxene (medium grey) on the right. The contact between olivine and pyroxene is clear but quite irregular. The whole sample is affected by fractures. Length of white bar = 1 mm.

Figure 5a (at right). Kalimashi Chrome Ore, as mined (BEI). The matrix, formed wholly of olivine (dark grey), contains magnetite (light grey), both as irregular zones and in finely disseminated form; the texture and structure of the minerals are indicative of the hydrothermal origin of the ore. Length of white bar = 0.1 mm. Microanalyses are shown for the whole area (**Fig. 5b**); magnetite (light grey area in **Fig. 5c**), and olivine (dark grey area in **Fig. 5d**).

5b



5c



5d

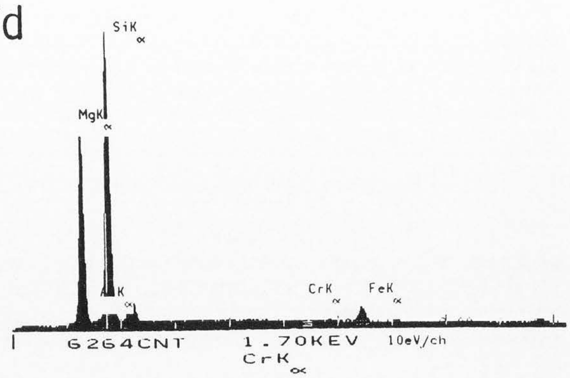


Figure 6. Kalimashi Chrome Ore: grain-size fraction between 250 and 500 micrometers after comminution (BEI). Grain texture and composition analysis reveals that marked interpenetration also exists in the comminution products. This sample contains calcite (phase A), which is practically absent in the ore and whose presence, when it can be found, is clearly of secondary origin (water circulation in fractured bodies). Length of white bar = 0.1 mm.

Table 2: Textural characteristics of chromium particles in the run-of-mine ore

Texture		Particle (%) Size class (mm)		
		-0.7+0.5	-0.5+0.3	-0.3+0.1
M	Massive	60.20	33.80	6.00
LND	Slightly Disseminated	42.10	40.90	17.00
D	Disseminated	15.00	34.15	40.85
FD	Finely Disseminated	20.50	33.20	46.30
LD	Linear	12.80	40.20	47.00

Table 3: Degree of liberation (%) of chromite from gangue with breakdown by size class and textures

Texture	(%)	Size class (mm)		
		-1.0+0.4	-0.4+0.1	-0.1
M	23.68	47.66	84.33	100.00
LND	20.54	37.52	75.27	99.50
D	23.62	34.78	72.56	99.00
FD	11.79	5.82	48.42	89.32
LD	20.37	42.44	81.22	100.00

characteristics) was then determined.

The degree of liberation of the chromite is not particularly high at standard treatment dimensions (see Fig. 6 as an example). The experimental results demonstrate that the characteristics of the comminution products can be predicted on the basis of knowledge of ore structure and texture (Tables 2 and 3).

A forecast of the degree of liberation can be made for each grain size class, as a function of the comminution process adopted. These minerals were found to be fine and intimately interlocked, thus requiring fine grinding for liberation (Bonifazi et al., 1990). Hence it is possible to establish the most appropriate separation process for each class and the results of the benificiation operation can be predicted.

Conclusions

SEM examination of the chrome ore has revealed textures and structures that are difficult to identify by conventional methods of investigation. It has also explained the difficulty of beneficiating Kalimashi chromite ore. More precisely, it has revealed the presence of microfractures and erosion, often with the redeposition of gangue minerals. This results in the production of many fine particles (microfractures, preferential lines of rupture) during the various stages of benificiation, and it leads to low values of liberation. The microfractures fillings indicate a high percentage of mixed particles even at the finest grain sizes.

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Discussion With Reviewers

F.E.Huggins: You mention the presence of hematite in association with serpentine. How was the presence of this phase established?
Authors: During the process of alteration the iron forms magnetite. When the quantity of oxygen is low the iron forms hematite, which in the alteration zone, is transformed into limonite. The presence of magnetite and limonite, as products of alteration, was determined by optical microscopy (reflected light) and diffractometric analyses.

F.E.Huggins: Is there any correlation between serpentinization or other alteration process, depth of the deposit, and the ease of chromite liberation?
Authors: There is no correlation between the serpentinization process and the depth of the deposit. This process is developed in the peripheric zone, in the contact rocks and in the areas where the tectonic is very pronounced. The degree of liberation, on the contrary, is strictly related to the serpentinization process: to high values of the alteration corresponds a greater value of liberation in the products resulting from comminution.

F.E.Huggins: It is stated that the chromite deposits form and accumulate as the result of crystallization of ore melt formed by limited partial melting of the upper mantle. How can such Mg-rich and Cr-rich melts be generated from melting of mantle material?
Authors: The deposit is formed from the partial crystallization of the magma. The ferromagnesian minerals of the spinel family of chromite and magnetite crystallize first, since these early minerals are more dense than the residual magma. Olivine alone produces dunite. Olivine and orthopyroxene together constitute peridotite, harzburgite and pyroxenite. When flow rates were highest only the dense high-specific-gravity oxides could settle and accumulate on the floor, and laterally extensive but thin layers of chromite rocks were formed; for these reasons the ore bodies are stratified. The concentration of chrome is not as high in the deposits of podiform type as Bulqiza and Batra ore bodies (Fig.7).

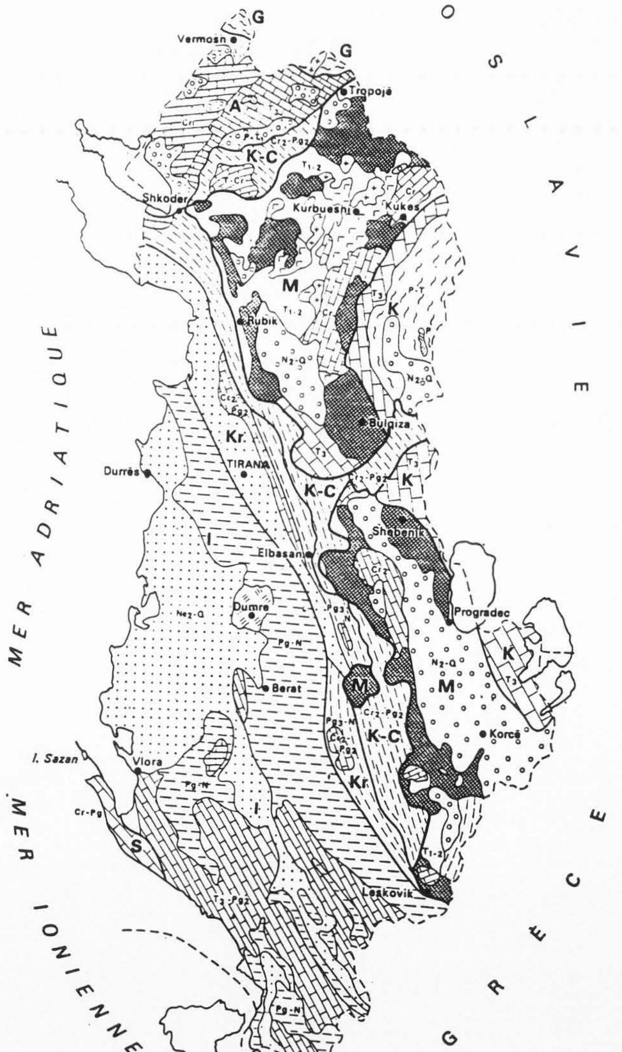

Figure 7. Geo-structural map of Albania (from the geologic map of Albania 1:200.000 of 1967 and from tectonic map 1:500.000 of 1969).

Internal Albanides

KORAB AREA-K: (N2-Q) molasse formation; (T3) carbonatic formation; (P-T) slate, evaporitic and detritic sequence; (D) evaporitic. MIRDITE AREA-M: (N2-Q) molasse formation; (T3) carbonatic formation; (T1-2) volcanic-sedimentary rocks, dolerite, aplite; (P) acids rocks; (M-R) mafic rocks; (UM-R) ultramafic rocks; Gash area-G (P-T) detritic sequence; (P) acids rocks.

External Albanides

ALBANIA ALPS-A: (Cr2-Pg2) flysch formation; (T3 and Cr) carbonatic formation; (P-Ti) terrigenous formation. KRASTA-CUKALI AREA K-C: (Cr2-Pg2) flysch formation; (T-Cr) cherty limestones. KRUJA AREA: (N2-Q) molasse formation; (Pg3-N) flysch formation; (Cr2-Pg2) carbonatic formation; Jonic area-J (N2-Q) molasse formation; (Pg-N) flysch formation; (T3-Pg2) flysch formation; (P) evaporitic; SAZAN AREA-S: (Cr-Pg) carbonatic formation.