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مطالعه تغییرات کرومیت توسط پراش اشعه ایکس: یک روش نیمه کمی

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چکیده: در این مطالعه سعی شده تا روابط بین کرومیت های آلتره و انواع غیر آلتره به کمک پراش اشعه ایکس تشخیص داده شود. برای این منظور مجموعه ای از نمونه های کرومیت های افیولیتی آلتره و غیر آلتره و همچنین تغییر شکل یافته و بدون تغییر شکل جمع آوری شده است. پیک های واضح و مضاعف به ترتیب از کرومیت های غیر آلتره و آلتره به دست آمدند. محاسبه پارامتر "a" کرومیت ها توسط مطالعات به روش پراش اشعه ایکس و همچنین محاسبه ترکیب همان نمونه ها به روش آنالیز مایکروپروب منجر به ترسیم نموداری شده که برای محاسبه مجدد نیمه کمی ترکیب کرومیت ها سودمند می باشد.

واژه‌های کلیدی: *دیفرکتوگرام اشعه X ، شبکه بلورین، حاشیه های آلتره کرومیت، پارامتر "a".*

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The XRD study of chromites modifications: A semi-qualitative approach

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Abstract: In this study we attempt to distinguish the relationship between the altered chromites and non-altered ones by X-ray diffraction. For the purpose of this study, an assemblage of altered/non-altered and deformed/non-deformed ophiolitic chromites has been collected and analyzied. Sharp and doubled peaks are resulted from non-altered and altered samples respectively. By using XRD studies, the parameter "a" from chromite grains has been calculated and the composition of same samples, obtaining from microprobe analysis, have given a chart that is useful for semi-qualitative recalculation of chromites composition.

Keywords: *Diffractograms, crystalline lattice, altered borders, parameter "a".*

Introduction

Chromites are accessory minerals in peridotites and in some cases concentrated to form chromitite deposits. This mineral is often used as an indicator of the petrogenetic environment of ultramafic rocks (e.g. [1-6]). Noted that chromites are highly susceptible to the modification during early hydrous alteration and/or subsequent metamorphism of host peridotites [7]. So, sub-solidus re-equilibrium, (e. g. [8-10]) and importantly the metamorphic modification (e.g. [11-17]) can complicate the petrogenetic interpretations based on the composition of chromites.

We will illustrate in this paper the modification of chromite grains based on the X-ray diffractograms and the resulted "a" parameter of chromites.

Method and materials

So samples of altered and non-altered chromite grains, have been analyzed by x-ray and numerous diffractograms were collected. Three types of ophiolitic chromites were involved in this study, residual chromites, podiform chromites and stratiform chromites [9, 18-20]. These chromites are either selected from altered and non-altered highly plastically deformed samples (residual and podiform chromites) and also altered/non-altered and non-deformed samples (stratiform chromites). Non-altered and non-deformed chromites are from Kizilyuksek Tepe unit in Pozanti-Karsanti massif in Turkey. This massif is located at the north of Adana and is composed of about 1500 meteres of dunitic cumulates associated with stratiform chromites [18,20]. Podiform chromites from Pozanti-Karsanti district that have suffered plastic deformation were also added. Altered and non-deformed samples are from Guleman massif, south of Turkey. This massif belongs to the Hatay-Kizildag belt [21]. In this massif, the chromites in stratiform units of Hamil-Vartinik, in a zone at the contact with metamorphic rocks (amphibolites) are highly altered and transformed into ferritchromite. The thickness of ferritchromite varies from 50 to 200 μm. Altered and non-altered residual chromites are both from Marmaris-Fethyie ophiolites and also from Antalya area. These residual chromite grains are disseminated in harzburgite tectonites and constitute of 1 to 3% of rock. Antalya massif is situated around Antalya gulf and is composed of mantle sequence, principally foliated harzburgites and of crustal sequence which consists of ultrabasic to basic cumulates. Marmaris-Fethyie massif is located at the southwestern part of Turkey and represents a complete mantle sequence. In this sequence, the alternation of lherzolite-harzburgite-dunite-websterite-pyroxenite can be distinguished. In addition, chromite grains were analyzed by microprobe at Nancy University, France. Acceleration voltage and Beam current were 15keV and 10nA respectively. Corrections have been calculated by ZAF program.

Discussion

In numerous cases, the observed diffractograms show the doubled or tripled peaks. Three reasons can be involved: 1- parasite reflections of Kβ radiation of Cu anticathode in X-ray tube. 2- reflection on the homologous planes of deformed areas 3- as double composition of chromites as the result of alteration processes in which they are composed of non-altered core and altered borders depleted in Al-Mg and enriched in Fe. The possibility of parasite radiations cannot be totally removed because twined peaks are often found and correspond to the reflections on (115) and (044) planes in chromites with relatively homogene composition associated to fresh rocks. So, concerning the second possibility that reflections on the homologous planes of cubic lattice must be showed by identical peaks, but deformed lattice can not reflect at the same manner on original homologous planes.

At least, in order to test this possibility a series of effective diffractograms was made from non-altered residual and podiform chromites deformed by plastic deformation. The diffractograms obtained from disoriented powder of these chromites show twined peaks. TEM observations show effective dislocations and junctions, and the respective indication of intracrystalline gliding, probably along [110] [9]. X-ray diffractions affected on two points of same crystals, therefore show some degree of rotations (generally 1 to 3 degrees, e.g. in samples FE06B and FE06C), (Table1).

The influence of altered borders of chromite on the twining of peaks is very clear. The ideal materials to demonstrate these phenomena are stratiform chromites in Kizilyuksek unit. Chromites were not affected at all by plastic deformation but the important variable is the opaque borders that could be observed. X-ray diffractograms obtained from purified chromites, i.e. MFK4 sample (Fig.1a), devoid of any altered border and do not show any twining on the (004) planes. These planes represent very intense peaks. On the other hand, chromite grains associated with MFK6 sample present relatively well-developed opaque borders (Ferritchromitization) and therefore give systematically twinned peaks (Fig.1b&c). Two diffractograms have been carried out; one of them is obtained from normal process, and is from grains selected and grinded by dense Clerici liquid (Fig.1b) and the other is from grains that are double crushed and passed from paramagnetic separation. The late process has been done to eliminate the altered ferritchromitized borders as much as possible (Fig.1C).

It can be effectively reported that very intense peak on the primary preparation is shifted toward small angles (Fig.1C). It corresponds to the elimination of altered borders of chromites. The control on the measurement precision of equal distance of different reticulate hkl planes has been provided by a standard, LiF (lithium Floride with $2\theta = 45.03$ on the (002)

plane). In Figure 2, parameter "a" of elementary lattice [$a = d_{hkl} \sqrt{(h^2+k^2+l^2)}$] has been obtained and it is a function of Al_2O_3 and Cr_2O_3 content, as well as the Cr/Al ratio of chromites. the paramenter "a" become, larger where the borders are depleted in Al_2O_3. It demonstrates that this variation reflects the modification of chemical composition of chromites that occurred during their alteration.

Alternatively, the application of some processes about intensively ferritchromitized chromites in sample GUL201 leads to a result that is contrary to previous results. The diffractogram peak is not necessarily twinned. Parameter "a" calculated from plane (004) is 8.245± 0.01 A. The representative point of this value is suitably placed on the straight line of regression (point FC on the fig.2). On the other hand, intensive decreasing of Al and Mg and importantly increasing of Fe^{+3} in the borders of these altered chromites (sample GUL201) do not correspond to the increasing of parameter "a" of elementary lattice of mineral.

Table 1 Measurement of crystallographic parameters of chromites by XRD.

sample	location	2θ(004)	d(A^0)	"a"(A^0)	No det	precision
MFK1	KIZILYUKSEK	43.85	2.063	8.252	-	-
MFK2	KIZILYUKSEK	43.60	2.074	8.296	2	0.003
MFK3	KIZILYUKSEK	43.55	2.076	8.306	2	0.005
MFK4	KIZILYUKSEK	43.70	2.07	8.280	2	000
MFK6	KIZILYUKSEK	43.70	2.070	8.280	4	0.020
MFK7	KIZILYUKSEK	43.65	2.072	8.288	2	000
MFK10	KIZILYUKSEK	43.70	2.070	8.280	2	0.020
258F	POZANTI-	43.80	2.065	8.260	2	000
502/2	KARSANTI	43.65	2.072	8.288	1	-
502/1	POZANTI-	43.68	2.072	8.288	2	0.004
KAR4	KARSANTI	44	2.056	8.236	2	0.004
KAR1	POZANTI-	44	2.056	8.236	2	0.008
GOTC	KARSANTI	43.50	2.078	8.312	-	-
KUYU	KARSANTI	43.63	2.073	8.284	3	0.001
MAR191A	KARSANTI	43.70	2.070	8.28	2	-
MAR191B	KARSANTI	43.70	2.070	8.28	-	-
IBO	POZANTI-	43.77	2.067	8.268	2	000
FE01	KARSANTI	43.70	2.070	8.285	1	-
FE02	MARMARIS	43.75	2.067	8.268	2	000
FE03	MARMARIS	43.70	2.070	8.285	2	000
FE06B	MARMARIS	43.90	2.0606	8.242	-	-
FE06C	FETHYIE	43.80	2.0651	8.2604	-	-
ULU18	FETHYIE	43.70	2.07	8.28	-	-
ULU14	FETHYIE	43.80	2.065	8.267	3	0.008
ULU22	FETHYIE	43.60	2.074	8.296	-	-
MAT2	FETHYIE	43.70	2.0696	8.285	2	0.009
CT52	ULUPINAR	43.75	2.067	8.269	-	-
GUL201	ULUPINAR		2.06	8.245	2	0.010
	ULUPINAR					
	ANTALYA					
	CIRALI					
	GULEMAN					

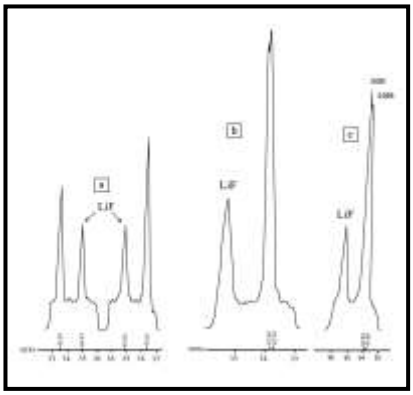

Figure 1 X-ray diffractograms obtained from non-altered chromites (a) and particularly altered (b and c) represent (004) planes.

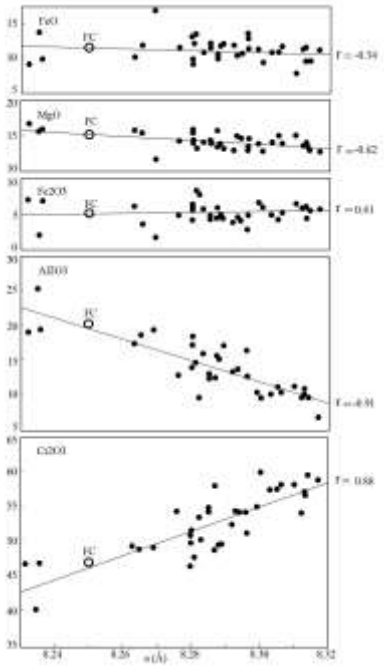

Figure 2 Variations of crystallographic "a" parameter as a function of the major elements content in chromites (see table 1). FC: ferritchromite. Taking into consideration that ferritchromite grain is related to an original grain, differ in composition from other samples shown in this diagram. Therefore the original and then altered grain as FC cannot be compared to other chromite samples plotted in diagram. This explains the apparent Al and Mg enrichment in diagram for FC grain, although these elements must be decreased during alteration.

Conclusions

X-ray diffraction can provide a simple way in order to study and compare the altered and non-altered chromite grains. The variations of crystallographic “a” parameter, as a function of the major element content of chromites, obtained from microprobe analysis. Therefore in order to estimate the composition of an unknown chromite grain, it is sufficient to determine the “a” parameter of chromite grain by XRD and then plot it on diagram 2. This is a semi-qualitative approach to calculate the chromites composition. Our study also shows that parameter "a" has not necessary increased in ferritchromite. This fact could be explained by the existence of vacancies. Al and Mg are highly dissolved and the significant substitutions of Mg by Fe^{+2} can also occur. This substitution doesn’t change the parameter of elementary lattice. Al dissolves and can fixes itself in chlorite or in septechlorite and Mg also can enter into the brucitic sheets. These secondary silicates are always associated with ferritchromites formation.

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