



Article

Ophiolite Chromite Deposits As a New Source for the Production of Refractory Chromite Sands

Micol Bussolesi ¹, Giovanni Grieco ¹, Alireza Eslami ² and Alessandro Cavallo ³,*

- Department of Earth Sciences, University of Milan, 20133 Milan, Italy; micol.bussolesi@unimi.it (M.B.); giovanni.grieco@unimi.it (G.G.)
- ² Institut des Sciences de la Terre, 38041 Grenoble, France; alireza.eslami@univ-grenoble-alpes.fr
- Department of Earth and Environmental Sciences—DISAT, University of Milan-Bicocca, 20126 Milan, Italy
- * Correspondence: alessandro.cavallo@unimib.it; Tel.: +39-3382343834

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Abstract: Chromite foundry sands, mixed with binding resins, are employed in the industry to form molds for high demanding casting of metals and steel. As there is no substitute, these sands highly contribute to placing chromium at the top value of the economic importance parameter in the EU classification of critical raw materials. Finding new sources to produce these sands can contribute to lowering their criticality. Chromite foundry sands must meet strict quality parameters, referred to as Cr₂O₃ content, Fineness Index, SiO₂ content, and Acid Demand. The foundry chromite market is dominated by South Africa production deriving from layered intrusion chromite deposits. Chromite sands from ophiolite chromite deposits, normally used for the metallurgical-grade chromite market, were tested as an alternative starting raw material to produce chromite foundry sands. The study of the silicate impurities assemblage showed that its mineralogy strongly affects the result of the most crucial parameter, the Acid Demand. Ophiolite chromite with serpentine impurities should be depurated to a hardly affordable 0.31% SiO₂ content to meet Acid Demand quality threshold, due to high reactivity of this silicate with acid environment of the test. Those with olivine impurities require to be depurated to a much more easily affordable 2.11% SiO₂ content. As a result, ophiolite chromite with an olivine dominated silicate assemblage can be used as an alternative source of chromite foundry sands.

Keywords: chromite foundry sand; ophiolite chromite; acid demand test; silicate mineralogy

1. Introduction

Chromite foundry sands, bonded with resins, are employed in the industry to form molds for casting metal and steel when high performance of sand is required (Figure 1A,B) [1]. They have special properties, such as high melting point $(2090\,^{\circ}\text{C})$, low thermal expansion and neutral chemical behavior that make chromite sands the best solution for high demanding casting [2] and are also the main reason why chromium has been included in the Critical Raw Material list [3].

Chromite foundry sands are generally mixed with binding resins and hardeners to produce molds. They substitute silica sands to cast metals with high density and high melting point and are much cheaper when compared to zircon sand [4]. They have to meet strict quality parameters in order to ensure a good final product [5]. The most important ones are Cr_2O_3 content (higher than 44%), Fineness Index (between 40 and 75), SiO_2 content (below 2.5%), and Acid Demand (below 10, 8, and 6 at pH = 3, 4, and 5, respectively). The Fineness Index (FI) is a measure of the grain size distribution of the sand and it must be neither too high (preventing degassing during casting processes) nor too low (resulting in an uneven surface of the final product). Low silica content is required in order to avoid chemical reactions between silicate impurities within the sand and the binding resins, which could

result in a decrease of the sand performance. As the reactivity of sand with resins is the most crucial parameter during casting, in addition to SiO_2 content, a specific test (Acid Demand Test, ADT) has been developed as a proxy of this process.

Foundry chromite production, a niche product in the chromite market but with a high added value, is almost completely dominated by South African companies, which provide the largest share of supply and the best foundry grade quality [6,7]. These chromites derive from layered intrusion-type deposits. Some chrome ore companies, however, started producing foundry sands from metallurgical-grade materials, coming from ophiolite-type deposits, widespread all over the world. While metallurgical-grade chromite is cheap and abundant, foundry sand grade is more expensive, as its high-quality parameters are much harder to attain. Thus it is profitable for such companies to further enrich metallurgical-grade ore to reach foundry grade quality [8]. As of April 2020, foundry chromite prices were between 380 and 540 \$/ton. Expanding the chromite foundry sand market to other producers can widely contribute to lowering the criticality of this commodity, and triggering local production.

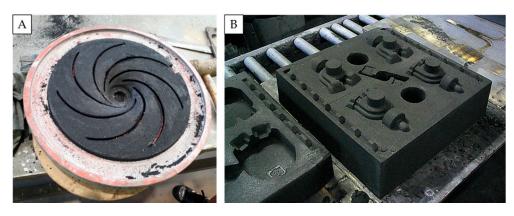


Figure 1. (A,B) chromite sand molds for refractory use (Flowserve Foundry, Desio, Italy).

The present work aims to provide new insights into the production of foundry chromite grade from metallurgical-grade chromite coming from ophiolite-type deposits. For this purpose, two chromite concentrates from ophiolite deposits in Iran and Greece have been tested and compared with South African chromite sands. The first one is a sand used in the Iranian foundry market, the second one is a metallurgical-grade chromite concentrate. These sands were selected as potential candidates to replace South Africa chromite sands in the European foundry market. As the most critical difference between layered intrusions and ophiolite-type deposits for the production of foundry sands is the different mineralogy of silicate impurities within the sand concentrate, we then focused on the different effects that these impurities have on ADT values. This would provide an important tool in the production of chromite foundry sands from metallurgical-grade ophiolite-type chromite deposits.

2. Materials and Methods

Analyzed samples include one commercial South African chromite sand provided by Laviosa Chimica Mineraria S.p.A, two chromite concentrates from chromite enrichment plants and four rock samples (orthopyroxenite, dunite, serpentinized dunite, and chloritized dunite) representative of different silicate impurities that can be found in chromite sands: orthopyroxene, olivine, serpentine, and chlorite. Moreover, two partially serpentinized dunites from the Aetoraches and Rizo mines have been selected and analyzed. These last two samples represent mixed serpentine-olivine assemblages that can be found within some ophiolite chromitites (Table 1). Concentrates where sampled directly from the separation plant at the mines in Aetoraches, Northern Greece, and Neyriz, Southern Iran. These mines exploit massive and disseminated chromitite bodies hosted in partially serpentinized peridotites of ophiolites [9–12]. Olivine and serpentine are the most common impurities in ophiolite chromite deposits and they often occur together in different proportions [13–15].

Sample	Locality	Sample	Major silicates	
SA	South Africa	Quality Proxy sand	Orthopyroxene	
AE	Aetoraches (GR)	Chromite sand	Olivine + Serpentine	
NE	Neyriz (IRN)	Chromite sand	Serpentine	
CHL	Abdasht (IRN)	Chloritized sample	Chlorite	
SRP	Neyriz (IRN)	Serpentinized sample	Serpentine	
OLV	Finero (IT)	Dunite sample	Olivine	
OPX	Ivrea Verbano (IT)	Orthopyroxenite sample	Orthopyroxene	
RI-2	Aetoraches (GR)	Serpentinized dunite sample	Olivine + Serpentine	
AE-2	Rizo (GR)	Serpentinized dunite sample	Olivine + Serpentine	

Table 1. List of samples and their location.

2.1. Grain Size Distribution

An important quality parameter of chromite sands is the Fineness Index, which is derived from grain size distribution analysis. Fineness Index values accepted for chromite foundry sands are comprised between 40 and 75 [16]. Grain size distribution is estimated using a sieve column, and Fineness Index is calculated through Equation (1):

$$FI = \frac{p_1 a_1 + p_2 a_2 + p_3 a_3 + \dots}{p_1 + p_2 + p_3 + \dots}$$
 (1)

where:

FI = Fineness Index;

p = percentage of material collected by a specific sieve;

a = sieve parameter (Table 2).

Grain size distribution was performed on chromite sands SA and NE. For crushed samples (CHL, SRP, OLV, OPX, RI-2, and AE-2) and for Aetoraches chromite sand (AE), a fixed FI (between 40 and 50) was assembled in order to have a comparison with samples SA and NE.

Table 2. Sieve parameters used to calculate FI [16].

Standard Column (µm) 1 Sieve Parameter (a) 3150 3 1600 5

800 11 630 18 400 31 315 38 200 52 160 66 100 102 80 130 50 210 bottom 300

2.2. XRD Powder Diffraction

XRD analyses were performed on silicate samples using a high-resolution X-ray powder diffractometer Panalytical X'pert Pro at the department of Earth Sciences of the University of Milan. This powder diffractometer is equipped with an incident beam monochromator, which separates the $K\alpha_1 1$ and the $K\alpha_2$ and can work with the Bragg Brentano geometry (divergent beam) as well as with a parallel beam geometry.

¹ Standard column DIM4188.

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2.3. X-ray Fluorescence

Chromite foundry sands were analyzed at the University of Milan Bicocca using energy-dispersive X-ray fluorescence (EDXRF, Panalytical Epsilon 3). Data were collected using the Omnian methodology, a standardless method which utilizes internal machine standards for the construction of a calibration curve. Calibration curves have been then corrected using five external standards, SARM8, SARM9, CHR-BHG, CHR-Pt, GR-55, and VV-4.

2.4. Acid Demand Test

The Acid Demand Test (ADT) is a titration method used as a proxy for sand-resin reaction potential. The Acid Demand value takes into account the amount of acid consumed at three different pH levels. The procedure, implemented by Laviosa Chimica Mineraria S.p.A. [5], is here reported:

Materials

- 50 g of foundry sand
- 50 mL HCl (0.1M)
- 50 mL NaOH (0.1M)
- Purified H₂O

Procedure

- Mix 50 g of chromite sand with 50 mL of HCl, stir for 5 min and let the solution rest for 1 h.
- Filter the solution adding H₂O until the solution reaches 250 mL.
- Measure the pH value of the solution.
- Add NaOH until the solution reaches pH 3, 4, and 5, taking note of the volume of NaOH consumed after each step.

Acid Demand Value

ADT values for the three pH levels can be obtained through Equation (2):

$$ADT_{pHn} = 50 - An * f (2)$$

where:

n = 3, 4, 5;

An =volumes of NaOH consumed to reach pH 3, 4, 5;

f =correction factor for HCl and NaOH, determined through blank tests.

The accepted limits for the ADT parameter are 10 at pH = 3, 8 at pH = 4, and 6 at pH = 5. In order to limit the grain size effect on the acid demand results, for the evaluation of the silicate gangue, a narrow range of Fineness Index (between 40 and 50) was chosen. Moreover, for the evaluation of silicate mineralogy effect on the ADT, pure silicate sands were used, and tests were performed at fixed SiO_2 values of 2.5 wt % in 50 g of sand, that is 1.25 g of SiO_2 . The amount of starting material was recalculated based on the SiO_2 content of each silicate mineral. The choice of the silicate samples was based on the most common silicate minerals of chromite deposits, which are pyroxene, olivine, serpentine, chlorite, or a mix of those.

3. Results

3.1. Fineness Index

Grain size distribution analysis was performed on standard South African sand (SA) and on chromite sands produced in the Neyriz enrichment plant (NE) (Figure 2). The resulting FI are 50 and 41, respectively. For Aetoraches, as the metallurgical-grade final concentrate has a FI that does not meet foundry sand limits, a chromite sand with a FI of ~44 was assembled.

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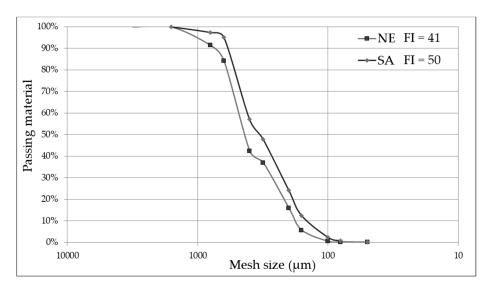


Figure 2. Grain size distribution of chromite sands from South Africa and from Neyriz.

3.2. Mineralogy of silicates

Silicate content in chromite concentrates was too low to be detected through x-ray diffraction and, for these samples, silicate minerals were recognized optically and through EDS spectroscopy. South Africa foundry sand mineralogy is dominated by orthopyroxene with minor amounts of plagioclase and olivine, which is the typical silicate assemblage interstitial to chromite grains in layered intrusion chromite deposits [17,18] (Figure 3A). Ophiolite chromitites, on the other hand, typically have a silicate matrix consisting of olivine [19,20]. Occasionally, diopside and pargasite can also be present in minor amounts [19,21]. These deposits are often subject to hydrothermal alteration, which causes primary silicates to be replaced by secondary ones, mainly serpentine and chlorite [19]. Carbonates within ophiolite chromitites are rare, and they are usually indicative of late hydrothermal processes [22,23].

Massive chromitites from the Vourinos complex, in which the Aetoraches deposit is included, are all partially serpentinized [24]. Within Aetoraches and the nearby Rizo deposit, the degree of serpentinization varies between 10 and 70%, and the silicate matrix is composed of serpentine and olivine in different proportions [25].

Massive chromitites from Neyriz deposit are composed of coarse-grained chromite with interstitial olivine, serpentine, and minor chlorite [12]. Disseminated ores show a silicate assemblage constituted by olivine and serpentine. Neyriz deposits show high degrees of serpentinization, up to 90% [12].

Both the Neyriz and Aetoraches samples show the typical silicate assemblage of ophiolite chromite deposits, dominated by olivine that can be totally (NE) or partially (AE) replaced by serpentine (Figure 3B,C) during retrograde metamorphism [26].

XRD analyses were performed on all the silicate samples, and qualitative results are reported in Figure 4. Samples show mineralogical assemblages dominated by serpentine varieties, chlorite, orthopyroxene, and olivine, respectively. Minor impurities are brucite, chromite, and pargasite in such low amounts that cannot affect the results of ADT. Aetoraches and Rizo serpentinized dunites (AE-2 and RI-2) also show an assemblage dominated by olivine and serpentine with minor chromite and clinochlore.

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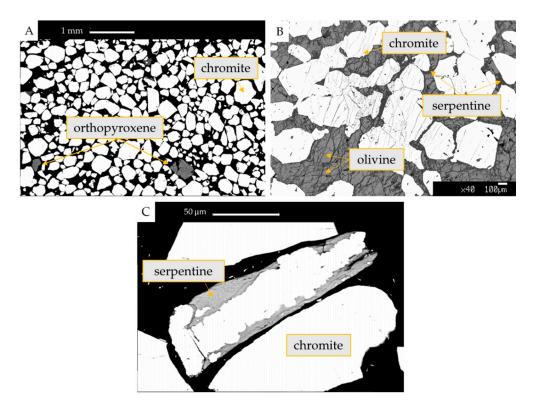


Figure 3. BSE images of **(A)** South Africa chromite sand, **(B)** massive chromitite sample from Aetoraches, **(C)** mixed serpentine-chromite grains in the Neyriz chromite sand.

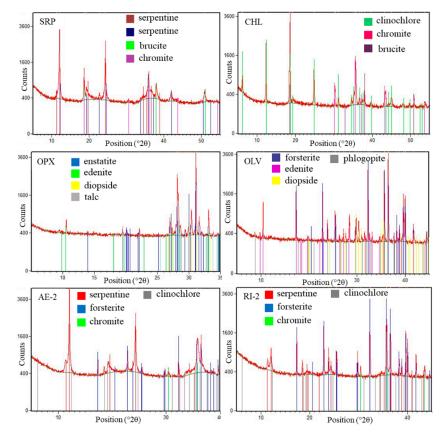


Figure 4. XRD patterns of silicate samples, sample labels as in Table 1.

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3.3. XRF

XRF analyses have been performed on the chromite concentrates. The results (Table 3) show that all three samples respect the Cr_2O_3 content threshold, with NE showing the highest Cr_2O_3 content of 56.27 wt%. Sample SA has the lowest SiO_2 content (0.70 wt%), followed by sample NE with a SiO_2 content of 2.01 wt%, both below the 2.5 wt% threshold. The only sample that exceeds the threshold is AE, with a SiO_2 content of 7.72 wt%, making this sand not suitable for foundry use.

Table 3. X-ray fluorescence results of chromite sands (wt%). Total Fe assumed as Fe₂O₃.

Sample	Cr_2O_3	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	TiO ₂
SA	44.66	0.70	14.52	0.14	29.07	9.88	0.19	0.68
NE	56.27	2.01	12.08	0.18	15.68	13.08	0.20	0.09
AE	48.90	7.72	7.17	0.33	19.46	14.74	0.24	0.12

3.4. Acid Demand

During beneficiation, silica impurities are mostly separated from chromite, and reported to the tailing material. To have a foundry quality, chromite sands need to have Acid Demand values at pH = 3, 4, and 5 not higher than 10, 8, and 6, respectively.

Acid Demand tests have been performed on chromite sands SA and NE, and on assembled chromite sand AE. In order to assess the behavior of different silicate impurities during Acid Demand, samples CHL, SRP, OLV, OPX, AE-2, and RI-2 have also been analyzed. Considering a SiO₂ limit of 2.5% in chromite foundry sands, the test was performed on the amount that would correspond to 2.5% SiO₂ within 50 g of a chromite sand, based on the silicate mineral chemistry (Equation (3)) (Table 4).

$$100(\%) : Y(\%) = x(g) : 1.25(g)$$
(3)

where:

Table 4. Acid demand test results of chromite sands and silicate samples.

Sample	Sand (g)	SiO ₂ (%)	Initial pH	ADT pH3	ADT pH4	ADT pH5
SA	50	0.70	1.52	8.9	6.6	6.0
NE	50	2.01	1.42	21.7	20.2	19.6
AE	50	7.7	2.62	40.7	33.3	32.3
CHL	4.12	2.5	1.93	23.5	20.8	20.2
OPX	2.09	2.5	1.78	3.6	1.1	0.4
OLV	3.19	2.5	1.70	10.6	8.6	7.9
SRP	2.88	2.5	2.20	39.2	36.4	36.03
AE-2	50	2.5	1.83	19.0	15.6	15.0
RI-2	50	2.5	1.87	16.7	13.4	12.8

100(%) = total of the sand

Y (%) = % SiO₂ within the silicate mineral

X(g) = grams of sand to use for acid demand test

 $1.25(g) = grams of SiO_2$ allowed within 50 g of foundry sand (2.5%)

4. Discussion

Chromite sands for foundry use have to meet all four quality parameters (FI, Cr_2O_3 , SiO_2 and ADT). South Africa (SA) sand, as expected, being the reference material for foundry market, meets all the required parameters. Neyriz (NE) chromite sand has a very high Cr_2O_3 content, a suitable grain size distribution and silica content lower than 2.5%. However, the acid demand values exceed the

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limits for all three pH (Figure 5). Aetoraches (AE) sand meets only the Cr₂O₃ and FI parameters. Silica content is much higher than the threshold and the ADT is around four times the threshold for all pH.

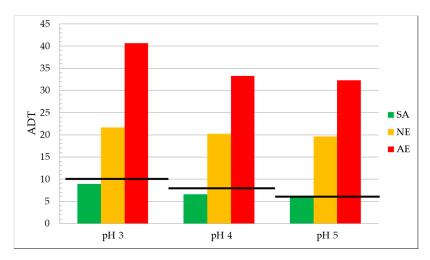


Figure 5. ADT values at pH = 3, 4, and 5 of chromite sand concentrates from South Africa, Neyriz and Aetoraches. Black lines represent ADT limits at each pH (labels as in Table 1).

The results on Aetoraches sand show that a typical metallurgical-grade chromite sand, with a Cr_2O_3 content around 48 wt % derived from ophiolite chromite deposits, is very far from meeting quality parameters for foundry use. The Neyriz sand, a substitute of unavailable South African sand in Iran, underwent a much deeper separation process in order to decrease SiO_2 content till meeting foundry sand quality. Our results show that the most demanding parameter is Acid Demand that is not met by NE sample in spite of its low SiO_2 content. This makes such sand unsuitable for the very demanding world foundry market.

If the high acid demand for Aetoraches sand is to be expected due to its high silica content, Neyriz acid demand values are more puzzling. The low difference in silica content between NE and SA cannot explain the high difference in Acid Demand values between the sands.

The lack of linear correlation between SiO₂ content and acid demand values can be explained by the different reactivity of silicate minerals in the acid environment of the test. All the three chromite sands have been enriched through gravity methods, and their silica content ranges from 0.70 wt% (SA) to 7.7 wt% (AE). Acid Demand tests on pure silicate samples of chlorite, serpentine, olivine, pyroxene (Table 4) at a fixed silica content of 2.5% show a very different reactivity of the minerals (Figure 6). For all pH values, the orthopyroxene gangue respects ADT limits, classifying as the least reactive mineral and, therefore, the best one (Figure 6). This explains why South African sand is the most performing one, as its gangue is mostly composed of orthopyroxenes. Olivine performs worse than orthopyroxene, but exceeds the ADT limits at pH 3, 4, and 5 by a tiny amount. The worst performing silicate sands are chlorite (CHL) and serpentine (SRP), which are high above the ADT limits.

Acid demand tests performed on two mixed serpentine-olivine samples at 2.5% SiO₂ content (Table 4, Figure 7), show ADT values comprised between those of pure olivine and pure serpentine. Sample RI-2 performs slightly better than sample AE-2, due to a lower degree of serpentinization. Both samples exceed the ADT limits for all three pH, however, they show values more similar to pure olivine than to pure serpentine. This means that the degree of serpentinization in the two samples is very low, and that a better constrain of the behavior of serpentine and olivine sands during Acid Demand tests could be pivotal for the production of chromite foundry sands from ophiolite chromitites.

The study of silicate mineralogy has a direct impact on the beneficiation processes of chromite sands. To produce chromite sand of foundry quality, enrichment plants must set machinery based on the mineralogy of the silicate assemblage. Orthopyroxene, a common silicate within layered intrusion

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chromite deposits, always respects the ADT limit for silica contents lower than 2.5%, so that when the sand meeting the SiO₂ quality parameter is produced, it will always meet also the ADT limits.

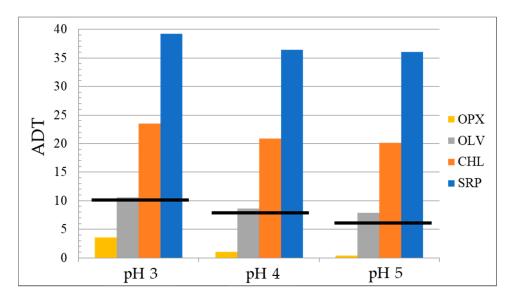


Figure 6. ADT values at pH = 3, 4, and 5 for pure silicate gangues (orthopyroxene, olivine, chlorite, and serpentine).

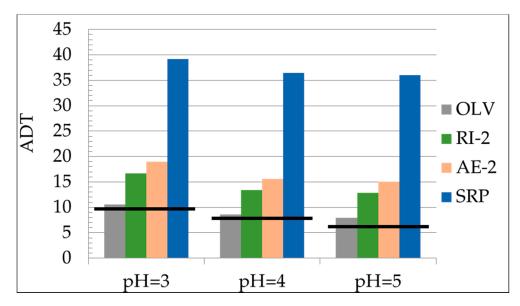


Figure 7. ADT values at pH = 3, 4, and 5 for mixed olivine-serpentine silicate gangues in Aetoraches and Rizo.

The results show that ophiolite chromites dominated by a chlorite or serpentine silicate assemblage cannot be enriched till meeting the foundry sand quality parameters. Hence, the possibility to produce foundry sand from these chromite deposits is limited to those with an olivine or mixed olivine-serpentine silicate assemblage that is quite common. In the following section, we focus on the impact of olivine and serpentine contents on the ADT value, in order to assess the maximum serpentine content of olivine-serpentine chromite sands that can be successfully enriched till foundry sand quality. For this purpose, two additional tests were performed (Table 5):

(i) Olivine and serpentine sand mixes at different proportions (25%, 50%, and 75% of serpentine) maintaining a fixed 2.5% of SiO₂, in order to simulate the behavior of partially serpentinized sands.

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(ii) Pure olivine and pure serpentine sands at SiO_2 contents lower than 2.5% (1.875%, 1.25%, and 0.625%).

Mixed olivine-serpentine samples show ADT values (Figure 8) comprised between the two pure end-members.

Table 5. Acid demand test results of mixed olivine-serpentine sands at fixed silica content and pure
olivine and pure serpentine sands at different silica contents.

Sample	SERP (g)	OLV (g)	SiO ₂ %	Initial pH	ADT pH3	ADT pH4	ADT pH5
25-75 SRP-OLV	0.76	2.28	2.50	2.03	30.5	27.2	26.6
50-50 SRP-OLV	1.52	1.52	2.50	2.11	33.5	30.7	30.2
75-25 SRP-OLV	2.22	0.74	2.50	2.15	36.2	33.3	32.6
25-SRP	0.72	0	0.63	1.65	24.4	22.2	21.6
50-SRP	1.44	0	1.25	1.83	32.1	29.7	29.0
75-SRP	2.16	0	1.88	1.88	36.9	34.7	34.3
25-OLV	0	0.80	0.63	1.45	5.9	4.3	4.0
50-OLV	0	1.60	1.25	1.48	7.8	6.1	5.8
75-OLV	0	2.40	1.88	1.46	8.7	6.9	6.4

For mixed olivine-serpentine, an average between antigorite and forsterite SiO_2 contents has been calculated.

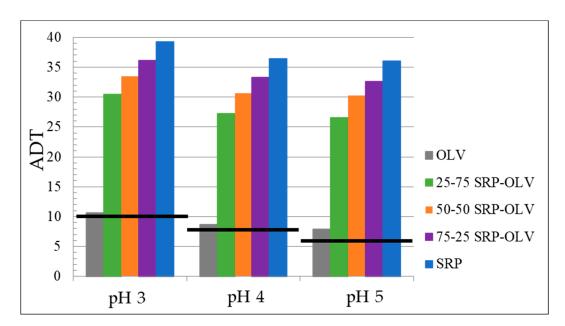


Figure 8. ADT values at pH = 3, 4, and 5 for mixed serpentine and olivine silicate assemblage (labels as in Table 1; Table 5).

ADT and serpentine modal contents (Figure 9A) are not in a linear correlation, and even a small amount of serpentine leads to high ADT values, so that the mix serpentine-olivine at 25% serpentine fraction has ADT values more similar to the ones of pure serpentine than of pure olivine. The highest SiO_2 contents that can result in a sand meeting the Acid Demand quality parameter can be calculated separately for olivine and serpentine from the results shown in Figure 9B.

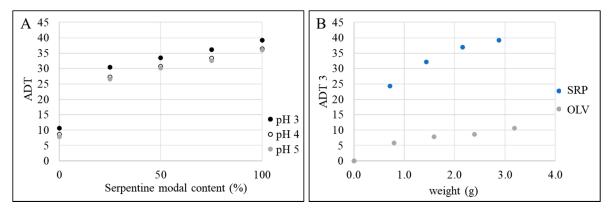


Figure 9. (**A**) ADT vs. serpentine modal content in a mix of serpentine and olivine sands at SiO_2 2.5%, at pH = 3, 4, and 5, (**B**) ADT at pH = 3 vs. weight of material (g) for pure olivine and serpentine sands.

The ADT parameter depends on the initial pH of the sand. As serpentine and olivine behave as bases, the initial pH is calculated from the equation of base dissociation constant (Equation (4)):

$$pH_i = 14 + \frac{1}{2}(\log_{10} Kb + \log_{10} Cb)$$
(4)

where:

 pH_i = initial pH of the sand

Kb = base dissociation constant

Cb = concentration of the base in the solution

As a consequence, ADT must be correlated by a base 10 logarithmic function to the amount of silicate added during acid demand test. Due to the fact that in absence of silicates the ADT value is necessarily 0, the logarithmic curve was transposed by factor 1 on the x axis as a mathematical artifact necessary to get finite values. ADT and the base 10 logarithm of w + 1, where w is the amount of silicate added (serpentine or olivine) have been then plotted (Figure 10) and show a linear correlation with high r^2 values. The ADT and the amount of silicate are correlated through the following relation (Equation (5)):

$$ADT = k * \log_{10}(w+1) \tag{5}$$

where:

k =coefficient of proportionality derived from the correlation;

w = amount of added silicate.

In order to estimate the amount of silicate that corresponds to the ADT3 threshold, we can substitute ADT = 10 in Equation (5). The results are 0.36 g of serpentine and 2.70 g of olivine. Finally, from the mass of silicate we can calculate, through the SiO_2 content of the mineral, the corresponding SiO_2 content of the chromite sand, that is 0.31% for serpentine and 2.11% for olivine.

These results mean that an ophiolite chromite with an only serpentine silicate assemblage should be purified to a final SiO_2 content as low as 0.31% to reach the ADT quality threshold, while an ophiolite chromite with an only olivine silicate assemblage should be purified to a much more easily affordable final SiO_2 content of 2.11% to reach the ADT quality threshold. For chromite sands with mixed olivine-serpentine assemblage, the serpentine works as a limiting factor as it is much more reactive than olivine, so it should anyway never exceed 0.36 g within the 50 g of chromite sand used in the test. That is less than 0.72% of serpentine in the sand, independently of the olivine content.

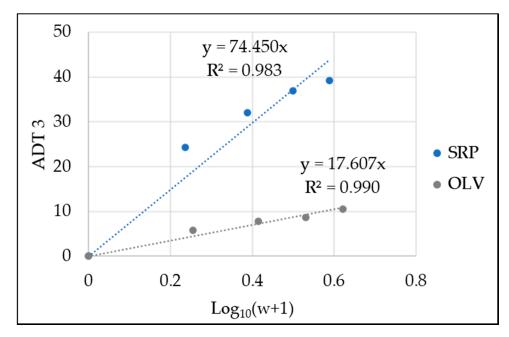


Figure 10. Linear correlation between ADT values at pH = 3 and log_{10} of the weight (g) of material used for the tests.

5. Conclusions

Chromite foundry sand is a crucial commodity, irreplaceable in high demanding casting of steel and metals. The identification of new possible sources for the production of such commodity can dramatically decrease the criticality of chromite raw material. Ophiolite chromite concentrates do not meet the required quality parameters, and also refractory sand produced in Iran from ophiolite chromites does not respect the most critical parameter, that is Acid Demand value. This is due to the different mineralogy of the silicate assemblage of these sands when compared to South African ones. The presence of serpentine, even in small amounts, due to its high reactivity with acid, precludes the possibility to get acid demand values respecting the quality threshold. On the other hand, olivine, the other most common silicate in ophiolite chromites shows a performance close to that of orthopyroxene, the best performing silicate, abundant in layered intrusion chromites, like those of South Africa.

The present work shows that the production of chromite foundry sands starting from ophiolite chromites is possible, but only for those where the silicate impurities assemblage is dominated by olivine, with very low or negligible amounts of serpentine. Two examples of ophiolite chromities with a low degree of serpentinization are reported in the work. Both Aetoraches and Rizo exceed the Acid Demand thresholds by a low amount, and an affordable degree of purification could lower the ADT values and make them suitable for the foundry market.

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References

- 1. Carey, P. Sand/binders/sand preparation and coremaking. Foundry Manag. Technol. 2002, 130, 39–52.
- 2. Surekha, B.; Hanumantha Rao, D.; Krishna Mohana Rao, G.; Pandu, R.V.; Parappagoudar, M.B. Application of response surface methodology for modeling the properties of chromite-based resin bonded sand cores. *Int. J. Mech.* **2013**, *7*, 443–458.
- 3. Annual Report 2014: Report on Critical Raw Materials for the EU; European Commission: Brussels, Belgium, 2014.
- 4. Bengulur, S.; Darwada, H.R.; Gurram, K.R.; Vundavilli, P.R. Experimental Studies on Properties of Chromite-based Resin Bonded Sand System. *Recent Adv. Robot. Aeronaut. Mech. Eng.* **2013**, 230–238.
- 5. Acid Demand 2008; Laviosa Chimica Mineraria s.p.a.: Livorno, Italy, 2008.
- 6. Kogel, J.E.; Trivedi, N.C.; Barker, J.M.; Krukowski, S.T. *Industrial Minerals & Rocks: Commodities, Markets, and Uses*; SME: Southfield, MI, USA, 2006.
- 7. Koleli, N.; Demir, A. Chromite. Environ. Mater. Waste 2016, 245–263.
- 8. Richard, P. Overview of the global chrome market. In Proceedings of the 1st Indinox Stainless Steel Conference, Ahmedabad, India, 25–26 January 2015.
- 9. Rassios, A. *Cooperative Development for Greek Chromite Reserves: Initial Review;* Institute of Geology and Mineral Exploration: Athens Greece, 2014.
- 10. Tzamos, E.; Kapsiotis, A.; Filippidis, A.; Koroneos, A.; Grieco, G.; Rassios, A.E.; Kantiranis, N.; Papadopoulos, A.; Gamaletsos, P.N.; Godelitsas, A. Metallogeny of the Chrome Ores of the Xerolivado-Skoumtsa Mine, Vourinos Ophiolite, Greece: Implications on the genesis of IPGE-bearing high-Cr chromitites within a heterogeneously depleted mantle section. *Ore Geol. Rev.* 2017, 90, 226–242. [CrossRef]
- 11. Ghorbani, M. Economic Geology of Iran: Mineral Deposits and Natural Resources; Springer: Berlin, Germany, 2013.
- 12. Rajabzadeh, M.A.; Nazari Dehkordi, T.; Caran, Ş. Mineralogy, geochemistry and geotectonic significance of mantle peridotites with high-Cr chromitites in the Neyriz ophiolite from the outer Zagros ophiolite belts, Iran. *J. African Earth Sci.* **2013**, *78*, 1–15. [CrossRef]
- 13. Grieco, G.; Bussolesi, M.; Tzamos, E.; Rassios, A.E.; Kapsiotis, A. Processes of primary and re-equilibration mineralization affecting chromitite ore geochemistry within the Vourinos ultramafic sequence, Vourinos ophiolite (West Macedonia, Greece). *Ore Geol. Rev.* 2018, *95*, 537–551. [CrossRef]
- 14. Grieco, G.; Merlini, A. Chromite alteration processes within Vourinos ophiolite. *Int. J. Earth Sci.* **2012**, 101, 1523–1533. [CrossRef]
- 15. Arai, S.; Yurimoto, H. Podiform chromitites of the Tari-Misaka ultramafic complex, southwestern Japan, as mantle-melt interaction products. *Econ. Geol.* **1994**, *89*, 1279–1288. [CrossRef]
- 16. *Terre e sabbie per fonderia: Campionamento e metodi di prova*; Ente Nazionale di Unificazione UNI462800: Milano, Italy, 1976.
- 17. McLaren, C.H.; De Villiers, J.P.R. The platinum-group chemistry and mineralogy of the UG-2 chromitite layer of the Bushveld Complex. *Econ. Geol.* **1982**, 77, 1348–1366. [CrossRef]
- 18. Mondal, S.K.; Mathez, E.A. Origin of the UG2 chromitite layer, Bushveld Complex. *J. Petrol.* **2007**, *48*, 495–510. [CrossRef]
- 19. Leblanc, M.; Nicolas, A. Ophiolitic Chromitites. Int. Geol. Rev. 1992, 34, 653–686. [CrossRef]
- 20. Mondal, S.K.; Griffin, W.L. *Processes and Ore Deposits of Ultramafic-Mafic Magmas through Space and Time*; Elsevier: Amsterdam, The Netherlands, 2017.
- 21. Augé, T. Chromite deposits in the northern Oman ophiolite: Mineralogical constraints. *Miner. Depos.* **1987**, 22, 1–10. [CrossRef]
- 22. Garuti, G.; Proenza, J.A.; Zaccarini, F. Distribution and mineralogy of platinum-group elements in altered chromitites of the Campo Formoso layered intrusion (Bahia State, Brazil): Control by magmatic and hydrothermal processes. *Mineral. Petrol.* **2007**, *89*, 159–188. [CrossRef]
- 23. Baccolo, L.P.; Grieco, G.; Bussolesi, M.; Eslami, A. Mineralogical study of rodingitized microgabbros and associated chromitite seams from the Nain ophiolite, Central Iran. In Proceedings of the EGU General Assembly, Vienna, Austria, 7–12 April 2019; Volume 21, p. 1.

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24. Rassios, A.; Tzamos, E.; Dilek, Y.; Bussolesi, M.; Grieco, G.; Batsi, A.; Gamaletsos, P.N. A structural approach to the genesis of chrome ores within the Vourinos ophiolite (Greece): Significance of ductile and brittle deformation processes in the formation of economic ore bodies in oceanic upper mantle peridotites. *Ore Geol. Rev.* **2020**, *125*, 103684. [CrossRef]

- 25. Cazzaniga, M. *Parametri tessiturali di qualità delle cromiti di Aetoraches e Rizo (complesso di Vourinos, Grecia)*; University of Milan: Milan, Italy, 2009.
- 26. Evans, B.W. The Serpentinite Multisystem Revisited: Chrysotile Is Metastable. *Int. Geol. Rev.* **2004**, *46*, 479–506. [CrossRef]



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