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Genesis and Multi-Episodic Alteration of Zircon-Bearing Chromitites from the Ayios Stefanos Mine, Othris Massif, Greece: Assessment of an Unconventional Hypothesis on the Origin of Zircon in Ophiolitic Chromitites

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Abstract: Several small chromium (Cr) ore bodies are hosted within a unit of tectonically thinned dunite in the retired Ayios Stefanos mine of the western Othris ophiolite complex in Greece. Chromium ores consist of tectonically imprinted bodies of semi-massive to massive, podiform and lenticular chromitites composed of chromian spinel [Cr-spinel] with high Cr# [Cr/(Cr + Al) = 0.51–0.66] and Mg# [Mg/(Mg + Fe²⁺) = 0.58–0.76], low Fe³⁺# [Fe³⁺/(Fe³⁺ + Fe²⁺) \leq 0.43] and low TiO₂ (≤ 0.21 wt %) content. This composition is characteristic of Cr-spinels in equilibrium with melts of intermediate affinity between island-arc tholeiites (IATs) and mid-ocean ridge basalts (MORBs). Several Cr-spinel crystals in these ores exhibit imperfect zones made up of spinel hosting oriented lamellae of Mg-silicates (mostly chlorite) locally overgrown by porous domains along grain boundaries and fractures. From the Cr-spinel core to the lamellae-rich rim Cr#, Mg# and Fe³⁺# generally increase (0.68–0.87, 0.78–0.88 and 0.55–0.80, respectively), whereas from the core or the spinel zones with oriented lamellae to the porous domains Mg# and Fe³⁺# generally decrease (0.45–0.74 and \leq 0.51, correspondingly). The lamellae-rich rims formed at oxidizing conditions, whereas the porous rims resulted from a later reducing event. Several tiny (\leq 30 µm), subhedral to anhedral and elongated Zr-bearing silicate mineral grains were discovered mainly along open and healed fractures cutting Cr-spinel. Most of the Zr-bearing silicate minerals (30 out of 35 grains) were found in a chromitite boulder vastly intruded by a complex network of gabbroic dykes. The dominant Zr-bearing silicate phase is by far zircon displaying a homogeneous internal texture in cathodoluminescence (CL) images. Raman spectroscopy data indicate that zircons have experienced structural damage due to self-irradiation. Their trace-element contents suggest derivation from a plagioclase-bearing, low-SiO₂ intermediate to mafic source. Combined micro-textural and minerochemical data repeat the possibility of zircon derivation from limited volumes of high-T fluids emanating from the gabbroic intrusions. Once zircon is precipitated in cracks, it may be altered to Ca-rich Zr-bearing silicate phases (i.e., armstrongite, calciocatapleiite). Almost all zircons in these samples show evidence of gains in solvent compounds (CaO, Al₂O₃ and FeO) possibly due to re-equilibration with late deuteric fluids.

Keywords: zircon; chromitites; ophiolites; metamorphism; Othris; Greece

1. Introduction and Rationale of the Study

Depleted sections of old sub-oceanic lithospheric mantle may contain substantial amounts of chromian spinel (hereafter Cr-spinel) in the form of single but sometimes economically valuable deposits of Cr (chrome ores) (e.g., [1]). Chromitites in ophiolites are predominantly dispersed at the transitional boundary between the Earth's crust and the mantle [2]. Despite their simple mineralogy, the mechanism that governs their genesis remains controversial. Interaction between mafic melts and peridotite wall rocks may change magma composition triggering Cr-spinel precipitation [3]. On the other hand, a growing body of work has concluded that focused flow and mingling of hydrous mafic magmas characterized by varying SiO₂-activities within 'dunite channels' (e.g., [4]) might be essential for the genesis of chromitites [5]. The inferred parental melts of most chromitites are thought to have arc-related supra subduction zone (SSZ) signatures (e.g., [6]). However, the 'coincidental' discovery of chromitite seams in peridotites from ultra-slow mid-ocean ridges (MOR) sends a cautionary message about the possibility of chromitite formation even in typical 'dry' environments [7,8]. Furthermore, it has been demonstrated that magmatic assimilation of a hydrated mantle protolith at Moho-level depths may dramatically affect the chemistry of a mid-ocean ridge basalt-type (MORB) melt causing increase of Cr concentration into economic ores [9]. Regardless of their origin, ophiolitic chromitites are widely considered as 'miniature time capsules' retaining priceless information on petrological issues of crucial importance such as: (i) the nature of the upper mantle [10]; (ii) mantle melting and subsequent melt extraction and interaction with peridotites [11] and lastly; (iii) recycling of the oceanic lithosphere [12]. Furthermore, Cr-spinel is widely regarded as a sensitive petrotectonic indicator because its composition is controlled by mantle melting processes that are typical of various geotectonic environments (e.g., [1,3,5,6]). The fundamental role of Cr-spinel and chromitites in resolving large scale petrological matters is reflected in their potential use to probe the differentiation processes in our planet's interior up to the Transition Zone (410–660 km) [13].

An increasing number of studies have revealed that both texture and composition of Cr-spinel in chromitites may be seriously affected by either prograde [14–16] or retrograde metamorphism [17,18] leading to a series of alteration products rich in FeO^t (and Cr_2O_3 at a lesser extent) and variably depleted in MgO and Al_2O_3 . These include high reflectivity (under reflected light), Fe²⁺- and Fe³⁺-rich phases commonly dubbed in the literature as ferritchromit/ferritchromite [19] or ferrian chromite [20].

A major breakthrough in our understanding of the subduction-driven recycling of the oceanic lithosphere was derived from the recovery of zircons (among other uncommon phases) from mantle-hosted podiform chromitites [13,21]. Several studies support that the zircon grains represent xenocrysts derived from the crustal part of a sinking slab [22–24]. However, a limited body of work has speculated that zircons may precipitate from fluid-rich metasomatic melts [25,26] or may be introduced to the chromitites via microscopic melt/fluid networks emanating from adjacent magmatic intrusions [27,28]. Hence, diverse processes may account for the discovery of zircon in chromitites but sometimes these processes may be acting in concert in a single mantle section [22].

In the present work we document the mode of occurrence, mineralogy and composition of chromitites from the area of Ayios Stefanos, Othris ophiolite complex, Greece. These observations aid the development of a model delineating the genesis and evolution of chromitites. This study reports our discovery of the existence of zircons in the Greek chromitites. Unraveling the origin of zircons delivers new insights into the nature and sequence of the petrologic processes that operated in the western branch of the Neo-Tethyan mantle. We supplement our investigation with new data on Cr-spinel and zircon alteration in an effort to acquire a more complete image of the processes affecting chromitites in the post-magmatic stage of lithospheric slab evolution.

2. Geological Background and Field Work

2.1. General Geological Framework—The Othris Ophiolites

The collision between Laurasia and Gondwana during the Jurassic and the Cretaceous led to the development of a lengthy suture zone that extends from Europe's mainland toward southeastern Asia. This suture zone is marked by numerous ophiolites representing remnants of the Neo-Tethys; the Neo-Tethys was a system of oceanic basins opening and spreading between a series of Cimmerian micro-plates during the Mesozoic-Early Paleogene [29]. The ophiolites of continental Greece constitute the southernmost part of the Dinarides-Hellenides sector of the Alpine Neo-Tethyan ophiolitic chain (Figure 1).



Figure 1. Distribution of ophiolites in the southernmost part of the Balkan Peninsula (modified after [30]). Key to lettering: V = Vourinos; P = Pindos; O = Othris (also marked by the open square). The initials F.Y.R.O.M. stand for Former Yugoslav Republic of Macedonia.

The Jurassic-aged Othris ophiolite complex (Figure 2) is comprised of a series of imbricated thrust sheets emplaced in reverse lithostratigraphic order onto the Pangean-derived Pelagonian continental margin [31,32]. From the top of the nappe pile to its base, the nappes consist of the following lithospheric sections: (1) plagioclase- and spinel-bearing lherzolites; (2) harzburgites; (3) 'near petrological Moho' peridotites including cumulate intrusions; (4) ultramafic and mafic cumulates; (5) sheeted dolerites as well as (6) pillow lavas and flows often including Cu mineralization related to ridgecrest hydrothermal activity. These ophiolitic nappes are obducted over the older (Permo-Triassic) Agrilia volcano-sedimentary sequence associated with rifting and sedimentation along the western margin of the Pelagonian micro-continent [33]. A chaotic lithological mixture of ophiolitic rocks and pelagic sediments in the area of Agoriani represents a remnant accretionary mélange forming part of the Avdella mélange [34]. Amphibolite outcrops near Lamia and Metalleion represent remnants of a sub-ophiolitic sole. Dating of these rocks using the ⁴⁰Ar/³⁹Ar isotopic pair yielded obduction initiation ages at 169 \pm 4 Ma [35].



Figure 2. Geological map of the Othris ophiolite complex [33].

2.2. Study Area, Sampling and Field Observations

Chromitites within Othris are relatively rare in comparison to other Neo-Tethyan ophiolites of Greece. Three inactive chrome (Cr) mines (Ayios Stefanos, Metalleion-Domokos and Tsangli-Eretria) produced approximately 1.5 Mt of ore until the early 1990s.

Ores of the retired Ayios Stefanos mine are almost completely exhausted. A few small $(1 \times 3 \text{ m})$, massive-textured chromitite bodies remain within a tectonically attenuated and highly serpentinized dunite-harzburgite ductile-brittle thrust zone (Figure 3a,b). This tectonic zone separates the plagioclase-bearing lherzolite-dominant nappe from the underlying harzburgite-dominant nappe that make up the Ayios Stefanos ultramafic unit. Twelve chromitite samples were collected from a chromitite boulder (~2 m³) within the quarry talus and four chromitite specimens were taken from a lenticular ore body (<1 m thick and a few m long; Figure 3c; Table A1 in the Appendix) 'trapped' within the reduced dunite-harzburgite deformed zone separating the peridotite nappes. The lenticular ore body is boudinaged and subcordant to the structural fabric (mylonitic foliation) of the hosting ductile-sheared peridotites. The contact between this chromitite body and the surrounding dunite leftover is sharp. The chromitite mine-talus boulder is massively intruded by a complex network of gabbroic dykes (\leq 15–20 cm-thick) infrequently hosting peridotite xenoliths (Figure 3c). Gabbroic intrusions are absent from the lenticular chrome ore body, but they occur within the tectonically sheared host peridotite within a surrounding zone of ~20 m. Several dunite micro-pods (\leq 5 cm across) were recognized in the lenticular chromitite. Both chromitites and peridotites appear highly serpentinized but otherwise almost non-weathered in terms of mesoscopic observation. The gabbro dykes in peridotites seem to have experienced variable degrees of rodingitization.

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Figure 3. (a) Geological map of the Ayios Stefanos region illustrating the bowing of structures synchronous to 'hot' nappe emplacement [36]; (b) The serpentinized dunite-harzburgite ductile-brittle thrust zone that separates the peridotite nappes in the Ayios Stefanos area; (c) A gabbroic dyke in the chromitite boulder within the quarry talus (this figure also appears in [36]). Abbreviations (in order of appearance): Cr = chromitite gallery (in b) and chromitite (in c); Sr = serpentinite; Gbr = gabbroic dyke.

3. Laboratory Methods

Polished thin sections of chromitites were examined using an OLYMPUS BX51 optical microscope (Olympus Optical Co., Ltd., Tokyo, Japan). A few Zr-bearing silicate mineral grains were discovered using conventional petrographic methods; however, their identification was hampered due to their limited size and low reflectance. For further mineral identification a CARL ZEISS SIGMA field emission-scanning electron microscope (FE-SEM) (ZEISS, Oberkochen, Germany) at the School of Earth Science and Geological Engineering (SESGE), Sun Yat-sen University (SYSU) was employed. Element maps of altered Cr-spinels and qualitative determination of Zr-bearing silicates were performed using energy-dispersive spectroscopy (EDS). The internal texture of the Zr-bearing silicates was studied at cathodoluminescence (CL) images using the same apparatus. To avoid effects of varying experimental conditions each grain was scanned for the same time and CL images were taken with constant signal amplification.

Quantitative analyses, line scanning and element maps of both altered spinel and Zr-bearing silicate mineral grains were performed using a three-detector JEOL JXA-8800R electron micro-probe analyzer (EMPA; JEOL, Tokyo, Japan) operating in the wavelength-dispersive spectroscopy (WDS) mode at the Electron Microprobe Lab, SYSU. Conditions for spinel analyses were 15 kV excitation voltage and 20 nA beam current with a beam diameter of 1 μ m. The peak and backgrounds counting times were 10 and 5 s, respectively, for the major elements. Spinels were analyzed using the K α line for Mg, Si, Ca, Al, Ti, V, Cr, Mn, Fe, Ni and Zn. Natural albite, diopside, Cr-spinel, rhodonite, ilmenite and metallic V, Ni and Zn were used as reference materials. The following diffracting crystals

were used: TAP for Al, Mg and Si, PETJ for Ca and Ti, and LIFH for Cr, Fe, Mn, Ni, V and Zn. The detection limits are listed in the following as parts-per-million [(ppm): mg/kg, 10^{-6}]: Mg = 100, Al = 108, Si = 118, Fe = 267, Ca = 174, Ti = 270, V = 199, Cr = 238, Zn = 486, Mn = 193 and Ni = 229. Both Fe^{3+} and Fe^{2+} in Cr-spinel were calculated assuming ideal spinel stoichiometry. Data were corrected with a ZAF [atomic number (Z); absorption (A); fluorescence (F)] correction calculation. Representative analyses of 'pristine' and altered spinels are given in Tables A2 and A3 (see Appendix). Analytical conditions for the Zr-bearing silicate minerals were 15 kV excitation voltage with a beam current of 20 nA. The electron beam was focused to a 1 µm spot to eliminate the spurious fluorescence effect from the neighboring phases. Counting times varied between 10 s (peak) and 5 s (background) for the K α line of Al, Cr, Fe, Mg, Mn, P, Ti, Hf and Si, the L α line of Ce, Pr, Y and Zr, and the M α line of Pb, Th and U. The reference materials included synthetic ZrSiO₄ (Zr, Si), HfSiO₄ (Hf), MgO (Mg), Al₂O₃ (AI), Y-Al garnet (Y), REE-glasses [rare earth elements (REE)], ThSiO₄ (Th) and UO₂ (U), natural apatite (P), wollastonite (Ca), rhodonite (Mn) and hematite (Fe). The TAP crystal was used for Al, Mg, Na, P and Si, the PETJ for Ca, Pb, Th, Ti, U, Y and Zr, and the LIFH for Ce, Cr, Fe and Hf. Since most of the analyzed oxides occur in trace amounts in the Zr-bearing silicate minerals, with the selected analytical conditions the following detection limits were achieved: $Al_2O_3 = 139$ ppm, FeO = 248 ppm, MgO = 121 ppm, CaO = 206 ppm, Na₂O = 130 ppm, Y_2O_3 = 418 ppm, ZrO₂ = 429 ppm, SiO₂ = 170 ppm, $Ce_2O_3 = 594 \text{ ppm}, HfO_2 = 1653 \text{ ppm}, UO_2 = 470 \text{ ppm}, ThO_2 = 711 \text{ ppm} \text{ and } P_2O_5 = 184 \text{ ppm}.$ The detection limits were automatically calculated by JEOL software taking into account the following parameters: (1) intensity of the characteristic X-ray of the analyzed element; (2) average X-ray intensity and (3) counting time of the background signal; and (4) element content in the standard material. The quantification of minor and especially trace elements by electron micro-probe may lead to analytical uncertainties (e.g., [28]). However, the precision and accuracy of minor and trace element measurements in zircon were evaluated by supplementary analyses performed on synthetic glasses and natural zircon standards. The applied acquisition conditions allowed high internal precision [Standard deviation (SD): \leq 3%]. Data were corrected with the CITZAF routine in JEOL software [37]. Representative analyses of the Zr-bearing silicate minerals are given in Table A4 (see Appendix).

The degree of radiation damage in 'zircons' Raman spectroscopy analyses was studied using a Renishaw inVia Raman Microscope (RENISHAW, New Mills, Wotton-under-Edge, Gloucestershire, UK) at the Confocal Laser Raman Spectrometry Lab, SYSU. Excitation was achieved using the 514 nm line of an Ar laser through a LEICA DMLM ×50 objective (LEICA MICROSYSTEMS, Wetzlar, Germany). The laser power was 5 mW and the collecting time 20 s. The scattered Raman light was collected in 180° back-scattering geometry and dispersed by a grating of 1800 grooves/mm. Spectra were acquired in the 50–1100 cm⁻¹ range with a resolution of 2 cm⁻¹. Analyses were performed as many μ m as possible away from the EMPA spots to avoid biased results due to structural changes caused by the electron beam. The parameters of the Raman bands are given in Table A5 (see Appendix).

4. Petrographic Investigation

4.1. Sample Characteristics

Chromitite within the lenticular body and the ore boulder consists of 60–95 modal % of mediumto coarse-grained Cr-spinel. Chromian spinel grains are smaller than 0.7 cm (in diameter), subhedral to euhedral showing amber to reddish brown color under transmitted light (Figure 4a). Some Cr-spinels show a pull-apart-like texture developed vertically to their long axis (Figure 4b). Chromian spinel fragmentation is common along brecciation zones (≤ 1 cm thick) within the chromitites. A thin section from the ore boulder was found to contain rutile. Rutile appears as transparent, white to yellowish (under reflected light), plate-like and more commonly rod-shaped 'inclusions' within Cr-spinel (Figure 4c). Rutile needles are fine-grained ($\leq 0.4 \mu m$ thick, $\leq 25 \mu m$ long) and developed in three crystallographic orientations (Figure 4c,d) indicating that they were exsolved from the Cr-spinel host as topotaxially aligned lamellae. The interstitial silicate matrix of the chromitites is entirely altered. Their mesostasis is composed of serpentine and chlorite with minor tremolite. Serpentine shows a pseudomorphic mesh texture after olivine. Occasionally bastites after orthopyroxene were found. Some bastites are pervasively cross cut by late serpentine veins (Figure 4e). Non-pseudomorphic serpentine textures (i.e., interpenetrating and hourglass; Figure 4f) were also recognized. Chlorite forms light brown blades intergrown with serpentine or brown to purplish aureoles surrounding Cr-spinel. Chlorite is the dominant filling phase in cataclastic zones and stretching planes of fractured Cr-spinel. Tremolite occurs as elongated grains showing a lepidoblastic texture. Late calcite veins (\leq 50 µm thick) are superimposed on all aforesaid structures in the chromitite boulder. Chromitites record limited evidence of near-surface weathering expressed in the form of red iddingsite aggregates.



Figure 4. Photomicrographs illustrating the petrographic characteristics of the Ayios Stefanos chromitites. (**a**) Reddish lobate Cr-spinel; (**b**) Chromian spinel displaying pull-apart-like texture (marked by the white arrows); (**c**,**d**) Rutile exsolutions developed in three crystallographic orientations $[Rt_{(a)}, Rt_{(b)}, Rt_{(c)}]$; (**e**) Bastite cut by late serpentine veins; (**f**) Serpentine showing hourglass texture. Abbreviations (in order of appearance): Chr = Cr-spinel; Srp = serpentine; Rt = rutile; Srp₁ = early serpentine; Srp₂ = late serpentine; PPL = plane polarized light; XPL = crossed polarized light; BSE = back scattered electron (image).

The Ayios Stefanos chromitites contain silicate minerals randomly distributed as inclusions in Cr-spinel. These are euhedral to subhedral and spherical in shape (Figure 4a). Inclusions range in size from several to 250 μ m. Silicate mineral inclusions comprise anhydrous (olivine, pyroxene) and hydrous [amphibole (edenitic pargasite) and Na-bearing phlogopite (aspidolite)] minerals; as well as their alteration products (chlorite and serpentine). Composite inclusions made up of orthopyroxene and amphiboles are the most common. A few olivine inclusions appear as negative crystals mimicking the symmetry of Cr-spinel. The negative-crystal faces of these inclusions denote that they might have grown along with the Cr-spinel host.

4.2. Micro-Structural Description of the Alteration Zones in Cr-Spinel

Chromian spinel grains may be partly surrounded by dark grey to black rims (Figure 5a); these rims are paragenetically associated with interpenetrating chlorite blades ($\leq 600 \mu m$; Figure 5b). Reflected light microscopy shows these rims to be more reflective than cores. Comparison of several BSE images of Cr-spinel grains with their equivalent photomicrographs indicates that the dark-colored rims correspond to bright zones in BSE images. The rim thickness ranges between 10 and 300 μ m, seldom reaching 500 µm. Rim boundaries with the intact cores are sharp and linear, but few appear irregular and diffuse. In extreme cases, the rim occupies almost the entire grain, leaving just a few isolated 'islands' of the original Cr-spinel (Figure 5c), this demonstrates that the rims do not represent overgrowths but products of Cr-spinel replacement. The rims display two internal structures. The first, which is easily discernible under low magnification, consists of porous/spongy spinel with chlorite as the sole pore-filling phase (Figure 5c,d). Infrequently, these pores exhibit a negative euhedral shape or they may be elongated ($\leq 200 \ \mu m$; Figure 5e,f). The second micro-fabric resembles the oriented chlorite lamellae texture in Cr-spinel described by [38]. Under low magnification this micro-texture appears as disordered aggregates of fine-grained spinel mixed with silicates (Figure 5g) but under high magnification has a net-like to diaplectic morphology. Careful observation shows that this micro-fabric is defined by a series of Mg-silicate lamellae ($\leq 3 \mu m \log p$) oriented parallel to one of four directions that correspond to the four {111} planes of the Cr-spinel host with lamellae in the fourth orientation appearing as sub-rounded patches (Figure 5h). The spatial recurrence of this structure points toward a growth control through crystallographic planes. Both micro-structures were recognized in the lenticular ore body (Table A1 in the Appendix). When both micro-textures coexist in a single Cr-spinel grain, the outer part of the rimming zone is always porous.



Figure 5. Cont.



Figure 5. Photomicrographs illustrating Cr-spinel textural modification. (a) Chromian spinel surrounded by a dark grey rim; (b) The same image in XPL showing that the rim is surrounded by chlorite; (c) Chromian spinel almost entirely replaced by a bright (spinel) phase; (d) Porous spinel for Cr-spinel substitution; (e,f) Spongy spinel displaying elongation of pores; (g) Cr-spinel with a boundary made up of spinel mixed with Mg-silicates; (h) Close up of the white, open square in (g) illustrating the oriented Mg-silicate lamellae micro-texture in Cr-spinel. The intersection of Mg-silicate needles in three directions is also marked. Abbreviations (in order of appearance): Fe-Chr = altered spinel; Chl = chlorite; Fe-Chr₁ = lamellae-rich spinel; Fe-Chr₂ = porous spinel; Hgr = hydrogrossular; the rest as in Figure 4.

4.3. The Zr-Bearing Silicate Minerals

4.3.1. Distribution, Paragenesis and Micro-Textural Relations

A total of 35 Zr-bearing silicate grains were discovered in 5 chromitite samples (Table A1 in the Appendix). Most of them (22 grains) were found distributed in narrow zones of about $400 \times 200 \ \mu\text{m}^2$, each grain is smaller than 30 μm across; grain size distribution is lopsided because most particles (80%) range between 10 and 15 μm . Four different zirconosilicate minerals were recognized; namely, zircon, armstrongite, calciocatapleiite and a Zr-bearing Mg-silicate phase. Under transmitted light, the largest Zr-bearing silicate grains appear as dark grey to murky-brown and translucent crystals with low interference colors. They are located within the following structural sites: (i) unaltered Cr-spinel cores commonly along restored fissures or cracks filled with secondary silicates (Figure 6a–c); (ii) altered Cr-spinel boundaries (Figure 6d) and (iii) cataclastic zones cemented by serpentine (Figure 6e,f).

Zircon (30 grains) forms subhedral to anhedral (Figure 7a) and elongated grains (Figure 7b), occurring as single grains or as intergrowths with pargasite (Figure 6a) or Ca-bearing Zr-rich silicates (Figure 7b,c). Some zircons exhibit across-grain thickness variations (1–10 μ m; Figure 7b,c). Zircons are located in fractures filled with chlorite and serpentine or placed along annealed micro-cracks (Figure 7c). Zircon in cataclastic zones probably represents wreckages of shattered grains (Figure 6e,f). The Ca-bearing Zr-rich silicates are small (<10 μ m), mottled and develop at the expense of zircons transected by open or healed cracks (Figure 7d–f).



Figure 6. Photomicrographs showing the micro-structural sites of zircons. (**a**–**c**) Zircon found along open or healed cracks in Cr-spinel; (**d**) Zircon hosted by porous spinel; (**e**,**f**) Zircon in cataclastic zones. Abbreviations: Zrn = zircon; the rest as in Figures 4 and 5.



Figure 7. Cont.



Figure 7. Photomicrographs illustrating the impact of alteration on zircons. (a) Subhedral, altered zircon in Cr-spinel; (b) Elongated zircon; (c) Intergrowth of zircon with calciocatapleiite; (d–f) Almost complete armstrongite for zircon substitution. Abbreviations (in order of appearance): $Zrn^* =$ altered zircon; Arm = armstrongite; Cpl = calciocatapleiite; Mg-Si* = unidentified Zr-bearing Mg-silicate; the rest as in Figures 4–6.

4.3.2. Cathodoluminescence Imaging and Element Distribution Maps

In CL images zircons appear to be dark and practically textureless, highly resembling metamict zircon (Figure 8a) [39,40]. Only in a few grains could some complex and irregular internal patterns be discerned (Figure 8b–e). All zircons have a strong BSE signal and suppressed CL emission (Figures 6–8). The Ca-bearing Zr-rich silicate grains yielded weak BSE and CL intensities being virtually non-luminescent in accordance with their hydrous nature (Figure 8f) [39].



Figure 8. Cathodoluminescence (CL) images of selected Zr-bearing silicate crystals. (**a**) Zircon (marked by the red, open square in Figure 6c) with nearly homogeneous texture; (**b**–**e**) Zirconium-bearing silicates with irregular texture [originally depicted in Figures 6f and 7a–c (in the last figure the imaged zircon is marked by a red square)]; (**f**) Armstrongite (originally depicted in Figure 7e) with very weak CL intensity.

Zircons with irregular internal texture commonly have crystal domains with weak CL response but higher Y_2O_3 and P_2O_5 contents compared to those with stronger CL emission, suggesting that both Y^{3+} and P^{5+} act as possible CL stimulators (Figure 9a,b). We note that various trace elements below the microprobe detection limit may also cause or suppress luminescence (e.g., [40]). Though it is known that the U-content of zircon may be qualitatively predicted via CL imaging [41] no differences in the amount of U were documented between areas of distinct CL intensity (Figure 9c). Element distribution maps and line scans revealed that a few zircon grains are cryptically zoned with decreasing abundances of major elements (Si, Zr and Y) from core to rim (Figure 9d–f); though it was not possible to detect which trace element(s) counterbalance this decrease.



Figure 9. (**a**–**c**) Single-element (WDS) X-ray maps of the zircon grain originally illustrated in Figure 6a; (**d**–**f**) Single-element (WDS) X-ray maps of the zircon grain originally illustrated in Figure 7c (marked by the red square). Line scans are also shown for the zircon crystal depicted in Figure 6a, where the beginning of analyses is marked by the dark blue circle. Abbreviations are as in Figures 4 and 6.

5. Mineral Chemistry

5.1. Spinel-Type Minerals

Electron microprobe analyses of Cr-spinels from the Ayios Stefanos ores (excluding Cr-spinel analyses from sample No. 6) show that their composition is rather heterogeneous (42.09–51.76 wt % Cr₂O₃, 16.55–27.13 wt % Al₂O₃ (Figure 10a), 12.28–16.91 wt % MgO and 12.32–18.75 wt % FeO^t) with Cr# [Cr/(Cr + Al)] values that range from 0.51 to 0.66, Mg# [Mg/(Mg + Fe²⁺)] values that vary between



Figure 10. Pristine Cr-spinel composition in terms of: (a) Al_2O_3 vs. Cr_2O_3 ; (b) Cr# [= Cr/(Cr + Al)] vs. Mg# [= Mg/(Mg + Fe²⁺)]; (c) TiO₂ vs. Cr# and (d) TiO₂ vs. Al_2O_3 (wt %). Fields for podiform and stratiform chromitites are from [42]. Fields for spinel in equilibrium with N-MORBs and boninites in (b) are from [43]. Fields for Cr-spinel in equilibrium with MORBs, IATs and boninites in (c) are from [44]. Compositional fields in (d) are from [45]. Abbreviations: (N-)MORBS = (normal) mid-ocean ridge basalts, IAT = island arc tholeiites, BABB = back-arc basin basalts; OIB = ocean islands basalts, LIP = large igneous province (basalts).

Chromian spinel in sample No. 6 has a quite different composition [Mg#: 0.44-0.50, TiO₂: 0.23-0.49 wt % (Figure 10c,d) and V₂O₃: 0.21-0.31 wt %] compared to Cr-spinel from the rest specimens. Rather than invoking primary magma source variation, this corresponds with the presence of rutile exsolutions from Cr-spinel in this sample; though, care was taken to avoid the exsolved rutile during the stage of microanalyses.

The lamellae-rich zones show limited variation in Cr_2O_3 (45.20–48.38 wt %), wide variations in Al_2O_3 (4.49–12.57 wt %), MgO (15.01–17.63 wt %) and Fe_2O_3 (11.48–19.00 wt %), high Cr# (0.71–0.87), Mg# (0.78–0.88) and Fe^{3+} # (0.55–0.80). The porous-appearing textural zones have a different composition (Cr_2O_3 : 43.71–62.43 wt %, Al_2O_3 : 0.55–21.96 wt. %, MgO: 8.89–16.17 wt %, Fe_2O_3 : \leq 16.68 wt %, Cr#: 0.58–0.99, Mg#: 0.45–0.74, Fe^{3+} #: \leq 0.51; Figure 11a,b) from the lamellae-rich zones. Selected 'intact' and altered Cr-spinel analyses are listed in Tables A2 and A3 (Appendix). The high Cr# values of the porous spinel zones resemble those of the chromite coronas and inclusions in the Maqsad (Oman) chromitites recently reported by [9] as well as those of Cr-spinel from boninites [43]. However, a striking difference is the very high TiO₂ content (up to 0.80 wt %) measured in the porous spinel domains. Furthermore, porous spinel may have much higher Fe_2O_3 contents than those reported for chromite coronas and inclusions in the Maqsad chromitites [9].



Figure 11. Variations of altered Cr-spinel in terms of: (a) Cr# vs. Mg#; (b) Fe³⁺# vs. Mg#. The composition of Cr-spinel is contoured at a nominal *T* of 1200 °C for olivine compositions from Fo₈₀ to Fo₉₆ [43]. Abbreviations as in Figure 5.

Particularly for the lamellae-rich zones, these variations imply removal of Al (Figure 12a,b) and slight addition of Fe (Figure 12c). The Cr content remains steady (Figure 12d) so that the removal of Al results in the apparent augmentation of the Cr# ratio. The Mg content 'seems' unchangeable from the Cr-spinel core toward the alteration rim (Figure 12e). The high SiO₂ content is due to the presence of silicates in micro-pore spaces (Figure 12f).



Figure 12. Single-element (EDS) X-ray maps on part of a Cr-spinel grain that displays oriented lamellae intergrowth texture.

5.2. Zirconium-Bearing Silicates

5.2.1. Zircon (Ideally ZrSiO₄)

Zircon contains 52.71 to 64.03 wt % ZrO₂ and 34.02 to 37.62 wt % SiO₂ (34 spot EMPA-WDS analyses). This composition deviates from the ideal stoichiometric formula as ZrO₂ content is low (Figure 13a). These zircon grains contain up to 3.46 wt % HfO₂, which is within the range of HfO₂ abundance for natural zircon (0.5–5.0 wt %) [46]. They also contain limited amounts of Y₂O₃ (\leq 1.21 wt %) and traces of P₂O₅ (\leq 0.43 wt %). The UO₂ and ThO₂ contents are quite low (\leq 0.28 wt % and \leq 0.26 wt %, respectively) and the PbO content even lower (\leq 0.14 wt %). Common impurities include CaO, Al₂O₃ and FeO^t.

The Al³⁺ proportion in zircon was found to be negatively correlated with that of Zr⁴⁺ (Figure 13b). This probably implies that Al³⁺ for Zr⁴⁺ substitution in the dodecahedral site may be possible through a charge balance mechanism. In contrast, the HfO₂/Y₂O₃ ratio is positively correlated with the ZrO₂/Y₂O₃ ratio (Figure 13c) as it is expected when incorporation of Zr, Hf and Y in zircon is dominated by the typical xenotime-type coupled substitution [(Y³⁺ + REE³⁺) + P⁵⁺ \leftrightarrow Zr⁴⁺ + Si⁴⁺]. Selected zircon analyses are listed in Table A4 (see Appendix).



Figure 13. Plot of major and minor element abundances in zircon in the following variation diagrams: (a) ZrO_2 vs. SiO_2 ; (b) Al vs. Zr at. %; (c) HfO_2/Y_2O_3 vs. ZrO_2/Y_2O_3 .

5.2.2. Ca-Bearing Zr-Rich Silicates: Armstrongite (Ideally $CaZrSi_6O_{15} \cdot 2.5H_2O$) and Calciocatapleiite (Ideally $CaZrSi_3O_9 \cdot 2H_2O$)

Only one armstrongite microprobe analysis was possible (grain in Figure 7d) owing to the small size and complex association of the mineral with zircon. The analyzed armstrongite has: 48.86 wt % SiO₂, 25.79 wt % ZrO₂, 7.95 wt % CaO, 3.60 wt % MgO, 3.57 wt % Cr₂O₃, 1.60 wt % FeO^t, 0.89 wt % HfO₂ and 0.47 wt % Y₂O₃ (Table A4 in the Appendix). The low analytical total implies the presence of OH⁻.

A single microprobe analysis of calciocatapleiite (grain in Figure 7c) was carried out owing to the same analytical limitations mentioned above for armstrongite. Calciocatapleiite has the following composition: 45.88 wt % SiO₂, 22.36 wt % ZrO₂, 14.58 wt % CaO, 4.93 wt % Cr₂O₃, 3.74 wt % MgO, 2.18 wt % FeO^t, 1.03 wt % HfO₂, 0.42 wt % Y₂O₃ (Table A4 in the Appendix). The Zr/Hf ratio (37.78) is higher compared to that of the intergrowing zircon (27.77) indicating considerable loss of Hf from zircon. The imperfect analytical total is probably due to the hydrous nature of the mineral.

6. Confocal Raman Microspectroscopy

According to group and symmetry theory, 12 Raman active modes are expected in zircon [47]. One of the most prominent peaks in Raman spectra from natural zircons is the mode at 1008 cm⁻¹ (B_{1g} -antisymmetric stretching vibration) that is due to internal vibration of the SiO₄ tetrahedrons. More internal modes are observed at: 975 cm⁻¹ (A_{1g}), 439 cm⁻¹, 296 cm⁻¹, whereas the external modes are detected at: 393 cm⁻¹, 356 cm⁻¹, 225 cm⁻¹, 214 cm⁻¹ and 202 cm⁻¹ [48]. Care in interpretation is required since a number of studies indicate that Raman modes change at conditions that will damage zircon structure [49].

Several Raman spectra were analyzed over different areas of the zircons. The bands of the Si-O antisymmetric stretching vibration at 1008 cm⁻¹ show a large wavenumber shift at 1002.7–1005.6 cm⁻¹ and their full-widths at half-maximum (FWHM) are at 10.09–14.54 cm⁻¹ (Table A5 in the Appendix). The bands of the symmetric bending vibration and the symmetric rotating vibration are observed at 438.05–439.56 cm⁻¹ and 352.1–355.4 cm⁻¹ (Figure 14a), respectively, and their FWHM are at 8.06–19.38 cm⁻¹ and 9.80–17.17 cm⁻¹ (Table A5 in the Appendix). Both Si-O stretching modes between 970 and 1010 cm⁻¹ can be observed in all Raman spectra. The degree of disorder in zircon is proportional to the FWHM of the v_3 (SiO₄) stretching mode, which can be linked to variations in the Si-O bond lengths [50]. In our case the FWHM values (Table A5 in the Appendix) show limited variation (Figure 14b) around the ~1008 cm⁻¹ peak.



Figure 14. (a) Raman spectra in the wavenumber range of 100–1025 cm⁻¹ for the studied zircons; (b) Spectra of zircons normalized to the height of the $v_3(SiO_4)$ stretching mode at ~1008 cm⁻¹.

The large width of Raman peaks, the decrease in phonon frequencies of $v_3(SiO_4)$ and the increase of FWHM (Table A5 in the Appendix) represent the impact of α -decay radiation damage on zircon (Figure 14a) [49]. Our data show that zircons experienced metamictization.

7. Discussion

7.1. Magmatic Stage of Lithospheric Slab Evolution

7.1.1. Extent of Subsolidus Re-Equilibration and Parental Melt of the Chromitites

The majority of chromitite samples are essentially monomineralic enabling us to consider that Cr-spinel composition remained nearly undisturbed at the post-magmatic stage of evolution after the termination of spinel-spinel re-equilibration (/homogenization). This is corroborated by the chemical similarity of Cr-spinels from the massive-textured samples implying originally high MgO abundance and low Fe_2O_3 content in Cr-spinel cores. These compositional signatures cannot be explained by subsolidus Fe-Mg exchange between Cr-spinel cores and olivine due to diffusive re-equilibration [51] as it was demonstrated by [9]. Re-equilibration between Cr-spinel and orthopyroxene in our samples should be even less pronounced. This is due to the limited abundance of interstitial orthopyroxene in the studied chromitites marking the point at which saturation of the intercumulus melt with Cr-spinel and olivine terminated. However, the conceivable compositional range of olivine (Fo \approx 91–96) surrounding Cr-spinel (Figure 11a) implies that if any re-equilibration phenomena occurred these were restricted to the Cr-spinel grain boundaries. We have also tested the extent of subsolidus exchange between Cr-spinel and the gabbroic dykes for the semi-massive chromitite samples taken from the ore boulder. We found out that significant exchange happened between the gabbroic dyke and the chromitite walls of the ore boulder that was intruded by the gabbroic dykes network. We actually noted that Cr-spinel composition in sample No. 6 (low Mg#, high TiO₂ and V₂O₃), which represents part of the ore boulder almost in contact with a gabbroic dyke, deviates from that of Cr-spinel in the rest samples (Figure 10b-d; Table A2 in the Appendix). The presence of magmatic titanite in the dyke means that it was crystallized from a TiO₂-rich melt, that is, more likely "MOR" related. Interaction (in the concept of chemical exchange) of this gabbroic melt with the chromitite triggered enrichment of Cr-spinel in TiO₂. The TiO₂ in excess was expelled from Cr-spinel in the form of rutile exsolutions.

Experimental studies of spinel-liquid equilibrium performed at low P (1 bar) have shown that the Al₂O₃ content and the FeO/MgO ratio in Cr-spinel depend on the concentrations of these substances in the chromitite-precipitating melt (e.g., [52]). Chromian spinel can be used to compute massive chromitites parental melt composition applying the empirical formulae suggested by [52]:

$$\ln(\text{FeO}/\text{MgO})_{Cr-spinel} = 0.47 - 1.07 \text{Al} \#_{Cr-spinel} + 0.64 \text{Fe}^{3+} \#_{Cr-spinel} + \ln(\text{FeO}/\text{MgO})_{melt}$$
(1)

where $(FeO/MgO)_{Cr-spinel} = FeO/MgO$ ratio in Cr-spinel, $Al\#_{Cr-spinel} = Al/(Cr + Al + Fe^{3+})$ ratio in Cr-spinel and $Fe^{3+}\#_{Cr-spinel} = Fe^{3+}/(Cr + Al + Fe^{3+})$ ratio in Cr-spinel and $(FeO/MgO)_{melt} = FeO/MgO$ ratio in melt. The Al_2O_3 and TiO_2 budget of the parental melt can be estimated using the logarithmic expressions developed by [53]:

$$(Al_2O_3)_{melt} = 4.1386 \ln(Al_2O_3)_{Cr-spinel} + 2.2828$$
⁽²⁾

where $(Al_2O_3)_{melt} = Al_2O_3$ in melt, $(Al_2O_3)_{Cr-spinel} = Al_2O_3$ in Cr-spinel, and

$$(\text{TiO}_2)_{melt} = 0.708 \ln(\text{TiO}_2)_{Cr-svinel} + 1.6436$$
 (3)

where $(TiO_2)_{melt} = TiO_2$ in melt, $(TiO_2)_{Cr-spinel} = TiO_2$ in Cr-spinel Equation (3).

Implementation of Equation (1) to Equation (3) shows that the parental melt had FeO/MgO ratio varying from 0.75 to 1.42, 14.08–15.94 wt % Al₂O₃ and up to 0.55 wt % TiO₂. Our results indicate that chromitites crystallized from melts that had an intermediate composition between that of high-Mg island-arc tholeiites (IATs: 11.4–16.4 wt % Al₂O₃) [54] and mid-ocean ridge basalts (MORBs: ~15 wt % Al₂O₃) [55]. The inferred parental melts bear resemblance to those reported for the high-Al chromitites from the (shallow) mantle section of Oman (Figure 15) [9,56].

Jurassic basalts with intermediate affinity between MORBs and IATs [known as medium-Ti basalts (MTBs)] have been described from the Agoriani mélange (group 2 volcanic rocks) in Othris [57] and represent an intriguing feature of the western Albanides-Hellenides ophiolite belt [58].



Figure 15. Plots of the calculated Al_2O_3 and TiO_2 contents of the parental melts in equilibrium with chromitites. The MORB and Arc lines are from [53] using data on spinel-melt inclusions in MORB and arc lavas reported by [45,56]. The range of Cr-spinel and the calculated melt compositions from the chromitites of the shallow and deep mantle section in Oman [56] are shown for comparison. Only data of chromitite samples not associated with gabbroic intrusions were used for computation.

7.1.2. Genetic Mechanism and Geodynamic Setting of the Ayios Stefanos Chromitites

A series of diverse models have been proposed to decipher the enigmatic presence of dunites-chromitites in ophiolites [3–9]. Chromitites of Ayios Stefanos are sited within a common mantle 'horizon' and exhibit sharp contacts with the surrounding attenuated dunite sheath: these appear as artefacts of the ductile deformation within the tectonically-thinned dunite-harzburgite zone. However, the serpentinized dunite clots within the lenticular ore body show that chromitites and dunite share the same origin. This is confirmed by the similarity in the expression of optical properties (i.e., extinction) between the mesh serpentine in the surrounding serpentinite (after dunite) and mesh serpentine in the clots.

The frequent presence of edenitic pargasite and aspidolite as inclusions in Cr-spinel may point toward a volatile-rich zone encountered by the rising melt that formed the chromitites; however, there is no indication for the existence of a volatile-rich zone in the Othris mantle suite. Phase equilibria experiments and thermodynamic considerations show that in the presence of a water-rich fluid phase the stability domain of coexisting pyroxene, amphibole, aspidolite and associated Cr-spinel is confined to *P* up to 200 MPa and *T* under 950 °C far below the conditions traditionally invoked to explain the formation of Cr-rich immiscible melts (e.g., [9]). Therefore, the presence of amphibole and phlogopite and/or aspidolite inclusions in Cr-spinel probably indicates the involvement of an alkali-bearing hydrous melt in the precipitation of the chromitites as it has been proposed by previous studies (e.g., [51]).

Chromian spinel analyses straddle the area between the fields of spinel in equilibrium with arc melts and MORBs (Figure 10b–d). Melts of MTB affinity may be produced in the mantle underneath nascent arcs or back-arc basins; however, it is '*unlikely that the Othris ophiolites formed in a back-arc basin'* [59]. The release of this type of melts in Othris has been ascribed to 8%–10% hydrous melting of rising depleted lherzolitic (/clinopyroxene-bearing harzburgitic) diapirs [60] (i.e., the Ano Agoriani diapir).

We are in favor of a mechanism that involves migrating (ultra-)mafic melts-harzburgite interaction followed by melt-melt mixing to explain the formation of the Ayios Stefanos chromitites (e.g., [44]). The idea that the Ayios Stefanos chromitites crystallized from melts migrating through the mantle is supported by their dunitic envelope relics, which are interpreted to be partly replacive in origin following dissolution of pyroxenes from the harzburgite (e.g., [4]) and partly cumulative after olivine addition (e.g., [3,6]). Furthermore, the (ultra-)mafic nature of the melts is supported by the common finding of negative crystals of olivine inclusions in Cr-spinel, which plausibly share the same origin with the Cr-spinel. We presume that small volumes of poor in Cr and oxidized permeating MTB melts initially interacted with the Ayios Stefanos mantle harzburgites to transform them into dunites and

modify their own composition by enhancing their SiO_2 content. Subsequently, mixing of these modified melts with the next inputs of (primitive) MTB melts moved the resultant hybrid MTB magmas (enriched in Mg, Cr and H₂O) into the liquidus field of Cr-spinel, promoting the precipitation of chromitites (e.g., [3,5,6]). Soon these melts started diversifying and the 'instant' changes in their composition were recorded in the wide range of Cr# values (0.51–0.66) in Cr-spinel even from a single ore body. Further evidence of the diversification of the melts could be the limited presence of orthopyroxene (preserved as bastite) merely in those chromitite samples composed of low Cr# (<0.60) Cr-spinel.

We emphasize the heterogeneous nature of the West Othris mantle unit composed of minor dunite, harzburgite and lherzolite and their plagioclase-bearing equivalents [61]. This lithological variability does not require that the western-most branch of Neotethys consisted of numerous small oceanic basins nor does it necessitate a Jurassic left-lateral strike-slip fault juxtaposing ophiolites from different domains [61]. We also highlight the geochemical diversity among the Othris harzburgites, including both abyssal [62] and arc-type harzburgites [63]; though the former are predominant. Judging from this compositional variability and the contrasting geochemical signatures of the parental melts of both chromitites (MTB-type melt) and TiO₂-rich gabbro intrusions (MORB-type melt) we cannot accept the customarily adopted model of a well-developed suprasubduction zone (SSZ) as the ideal geotectonic setting for the genesis of the Ayios Stefanos chromitites. It is likely that these chromitites record a stage of magmatism along a near-transform fault of a slow-spreading ridge [59,62]. Our model represents a simpler, perhaps more 'elegant', hypothesis explaining the genesis of the Othris chromitites.

7.1.3. An Inductive Reasoning Approach to the Potential Origin of Zircons

Three main scenarios have been proposed to explain the 'paradoxical' finding of Zr-rich phases in ophiolitic chromitites: (i) incorporation of ancient zircons in the sub-oceanic mantle by ascending fluids/melts as a result of deep subduction [22]; (ii) precipitation of Zr-dominant phases by rich-in-fluid melts related to mantle metasomatism (e.g., [64,65]) and (iii) introduction of zircon in chromitites through (a network of) intergranular fluids representing late fractions of igneous intrusions in the upper mantle [27,28].

Zirconium-rich minerals have never before been reported from the West Othris peridotites and petrogenetic signatures related to carbonatite metasomatism are missing from the entire massif. We also note that there is no structural imprint related to a phase of carbonatite metasomatism from a subduction channel within the West Othris ophiolite. Zircon is a stable phase in the upper mantle [66] but the petrological history of the West Othris mantle, encompassing various episodes of partial melting and metasomatism [67], would hardly permit zircon storage for a long time. The Ayios Stefanos zircons do not host mantle mineral inclusions, have no inherited cores, and more importantly, do not show signs of corrosion due to incipient reaction with melt. For this reason, it is hard to envision that zircons were entrained from the peridotite wall-rocks by migrating melts.

The zircons we discovered are small, unlike crustal or detrital zircons that can reach much larger sizes. They are neither prismatic nor rounded and appear practically featureless in CL images, lacking any pre-existing texture relics (i.e., oscillatory zoning; Figure 8). Zircons are entirely absent from the mesh-textured serpentinized groundmass; possibly entrapment of old inherited zircons in olivine could effectively protect them from the ambient environment [22]. The zircon-pargasite intergrowths in Cr-spinel are anhedral with a granular texture (Figure 6a) unlike those described by [68]. These features are not indicative of zircons that derive from the sedimentary lid or the cumulate pile of a downgoing slab undergoing amphibolite-facies metamorphism [68]. Xenocrystic zircons have been described from several chromitite occurrences over the globe [21–26]. We note that recycled zircons from the Tibetan (Luobusa, Dongqiao), Semail (Oman) and Ray-Iz (Urals) chromitites have complex internal structures and co-occur with various combinations of super-reducing ultrahigh-pressure (SuR-UHP) minerals without showing resetting of their U-Pb ages [22,26]. However, a SuR-UHP mineral assemblage is missing from the Ayios Stefanos chromitites and the studied zircons show metamictization at variable degrees.

Zirconium contents in Cr-spinel rarely exceed a few ppm [69] making it hard for zircon to exsolve from the Cr-spinel lattice. This is further corroborated by zircon distribution and morphology, and is inconsistent with the crystallographically controlled patterns commonly resulting from exsolution.

The solubility of zircon in melt increases with increasing *T* and decreasing SiO₂-activity [70], thus zircon may be a liquidus phase mainly in felsic and intermediate melts. Mafic magmas require an unrealistically high Zr abundance (>5000 ppm) to crystallize zircon [71], whereas they are capable of dissolving zircon upon their release. However, zircon in mafic settings may grow in small and secluded Zr-rich melt volumes far from the liquidus [72]. Recently, it was shown that a population of 'young' (100–110 Ma) zircons from the Luobusa chromitites [25] could derive from mixing between juvenile mantle-derived melts and a crustal component [26]. Those zircons show idiomorphic habits with strongly marked, narrow oscillatory zoning and prismatic inclusions of fluorapatite [25] unlike the zircons we discovered.

It is accepted that rodingitization-related fluids can serve as potential carriers of zircon (e.g., [73]). We, however, did not find zircon associated with rodingitization-derived minerals (i.e., hydrogrossular), and the presence of 'micro-rodingite' veinlets occurs solely in a single zircon-bearing chromitite sample (1a). This would preclude a metasomatic origin for the examined zircons. In addition, the Ayios Stefanos zircons have no OH⁻ content that is symptomatic of zircon settled by low-*T* fluids [74].

We found that the majority of Zr-bearing silicate grains (30/35) were located in samples taken from a chromitite boulder that is massively intruded by gabbroic dykes. It is not coincidental that most of these grains are located in open or healed fractures that cut Cr-spinel (Figures 6a–d and 7b–d). Mantle deformation can develop fractures in 'brittle' massive-textured chromitites [75] that commonly serve as fluid pathways. At relatively high *T* conditions such fractures may anneal owing to Cr-spinel grain-boundary migration, promoted during recrystallization and metamorphism [20]. Evidence for this comes from the observation of almost linear trails of zircon or silicate grains (Figure 7a,d,f), which could correspond to former Cr-spinel crystal boundaries or restored fractures. A number of annealed cracks end up in Zr-bearing silicate grains without cutting them (i.e., Figure 6b). This indicates that these grains and the associated secondary silicates were introduced into already solid Cr-spinel by a fluid/melt prior to annealing. The absence of oscillatory zoning in CL images also indicates equilibrium with a volatile-bearing fluid/melt at high *T* [76].

The zircons in the Ayios Stefanos chromitites have a compositional signature that differs from that of mantle zircons, but is quite similar to the trace-element signature of zircons reported from plagioclase-bearing, low-SiO₂ intermediate to mafic sources (Figure 16) (e.g., [77,78]). In the Y vs. U and Y vs. Th diagrams (Figure 16a,b) our zircon analyses plot on the overlapping compositional fields of zircons from mafic lithologies, dolerites, larvikites and granitoids, substantially deviating from the composition of kimberlitic and carbonatitic zircons. As shown on the Hf vs. Y diagram (Figure 16c) they plot in the fields II, III and IV, whereas most analyses plot outside of any known field for zircon composition because of their low Hf contents. Even in this case our zircon analyses bear similarity to those from mafic to intermediate and felsic sources. Most of them are characterized by low HfO₂/Y₂O₃ ratios and low Hf (<1 wt %) contents likewise early to late magmatic zircons [74] from mafic settings (Figure 13c) [27]. Alternatively, it can be said that these zircon analyses define a fractionation trend toward progressively more depleted-in-Hf compositions.

Though the gabbroic intrusions are missing from the lenticular chromitite, they crop out within a radius of less than 20 m away from this ore body and crack propagation in the mantle is known to provide a robust pathway for the transport of metasomatic fluids and melts over long distances [27,79]. Moreover, all zircons display textural and compositional similarities implying that they share a mutual history. The relatively small thickness of each gabbroic intrusion let us believe that their parental melts were rapidly consumed leaving behind small volumes of high-*T* fluids. We suggest that the zircons derive from limited proportions of moderately high-*T* gabbro-related fluids that were introduced into the chromitites via a complex network of micro-fractures, which seems to be pervasive to the Ayios Stefanos mantle suite. Regarding zircon survival, it has been experimentally demonstrated that

heat wave propagation from an igneous intrusion will completely dissolve and reprecipitate zircons in Zr-poorer lithologies many diameters of the plutonic body away and often 10^3-10^4 years after the intrusion event [80].



Figure 16. Trace element correlations for zircons. (**a**) Y (ppm) vs. U (ppm); (**b**) Y (ppm) vs. Th (ppm); (**c**) Hf (wt %) vs. Y (ppm). Fields in (**a**,**b**) are from [77]; fields in (**c**) are from [78] (I = kimberlites, II = ultramafic, mafic and intermediate rocks, III = quartz-bearing intermediate and felsic rocks, IV = felsic rocks with 'high' SiO₂ content, V = greisens, VI = alkaline rocks and alkaline metasomatites of alkaline complexes, VII = carbonatites).

A quite similar scenario has been proposed to explain the origin of zircons in the chromitites of the Tumut ophiolite complex in southeast Australia [27] and the Cedrolina chromitites in Brazil [28]. The zircons we studied bear some resemblance to those found in the Early Jurassic Finero alpine chromitites (western Alps) wherein zircon genesis was ascribed to direct crystallization from the melt that formed the Finero chromitites during the Early Jurassic [81,82]; those anhedral to subhedral zircons occur in interstitial positions between Cr-spinel and olivine and/or orthopyroxene [65], forming aggregates of up to four crystals [64]. The Finero zircons are inclusion-free with low CL signals, no internal texture and high Th/U ratios, thus resembling the zircons in the Ayios Stefanos chromitites [64,82]. However, the Finero zircons may be up to 600 μ m across and sometimes are found as euhedral inclusions in Cr-spinel and olivine, with low Y contents [64]. The Finero zircons are attributed to formation in relation to carbonatitic metasomatism, a pervasive phenomenon in the Finero phlogopite peridotite complex [65]. This carbonatitic imprint is, as we have noted, missing from the Othris ophiolitic rocks.

A remaining question could be: did the presumed gabbro-derived fluids carry any existing zircons (from the dykes) or did the zircons settle at the stage of chromitites being invaded by the fluids? In the absence of any isotopic data for these zircons it is not possible to provide a direct answer to this question; our textural data cannot rule out either hypothesis at this stage of study.

7.2.1. The Polyphase Cooling History of the Chromitites

In cumulate lithologies, such as chromitites, zoning in Cr-spinel may be due to reaction with the intercumulus melt. However, this scenario is not applicable to the chromitite samples examined herein as zoning in Cr-spinel can be better described as a replacement texture rather than as a typical crystal growth texture. For instance, neither of the two micro-structures recognized in zoned Cr-spinels resembles oscillatory zoning indicating disruption of the melt boundary layer around Cr-spinel and changing growth-rate [83]. On the other hand, none of them has a typical sieved to wormy appearance that are supposed to be characteristic of diffusion-controlled or diffusion-limited (cellular) growth processes due to constitutional supercooling of metals [83,84]. Furthermore, from the 'pristine' Cr-spinel core to the reworked rims the Cr# increases, which is against a growth origin or even a magma fractionation trend for both kinds of micro-textures recognized at Cr-spinel grain boundaries. Additional evidence that no reaction between Cr-spinel and a remnant intercumulus melt actually occurred comes from the conceivable forsteritic composition of the adjacent olivine (Fo \approx 91–96) [43]. Petrographic observations indicate that both structures do not represent diffusion-controlled growth textures [38]. In most cases the oriented Mg-silicates lamellae appear to preferentially develop at the boundaries not in the interior of the Cr-spinel grains, which is against their formation due to diffusion of components from the Cr-spinel lattice. In fact, petrographic evidence suggests that the zoning observed in Cr-spinel is not a primary feature; but a replacement texture obtained as a result of reaction that proceeded from the outside to the inside of the affected Cr-spinel grains [14,16–18,20]. A strong relationship exists between zoning in Cr-spinel and the degree of chloritization-tremolitization of the Ayios Stefanos chromitites. Furthermore, the discovery of clinochlore 'haloes' around Cr-spinel and the observation that clinochlore blades are cut by serpentine confirm that retrograde metamorphism predated oceanic alteration (e.g., [20]).

The preservation of two alteration micro-textures in Cr-spinel from Ayios Stefanos indicates that chromitites underwent a multi-stage history of lithospheric cooling. Two compositional trends linked to Cr-spinel modification were recognized: (i) a general increase in the Cr#, Mg# and Fe³⁺# related to the development of the lamellae-rich zones (Figure 11a) and (ii) an increase in the Cr# coupled with a general decrease in the Mg# and Fe³⁺# related to the formation of the porous texture (Figure 11b). The first trend is inexplicable since the loss of Al³⁺ is not coupled with Mg²⁺ loss; hence, it cannot be ascribed to Cr-spinel and olivine replacement by ferrous chromite and chlorite at reducing conditions [20] or to advanced subsolidus re-equilibration (i.e., down to 750–700 °C, $P_{\rm H2O} = P_{\rm Tot}$) [85]. The high Fe³⁺# values of the lamellae-rich zones favor their formation at oxidizing conditions. The second trend results from Cr-spinel or lamellae-rich spinel reaction with olivine and their replacement by porous spinel and chlorite at reducing conditions as confirmed by the general decrease in the Fe³⁺# from the cores and lamellae-rich zones to the porous rims (Figure 11b).

Computation performed in the closed system Cr_2O_3 -MgO-Al₂O₃-SiO₂-H₂O (CrMASH) rules out the formation of ferrian chromite and chlorite by reaction between Al-spinel and serpentine [20]. Thermodynamic predictions in the fluid-saturated system Cr_2O_3 -MgO-FeO-Al₂O₃-SiO₂-H₂O (CrMFASH) do not exclude direct breakdown of Al-spinel to chlorite and ferrian chromite after reaction with MgO- and SiO₂-rich fluids [86]. The lamellae-rich zones probably formed in this way according to a modified version of the equation proposed by [87]:

$$MAl_{2}O_{4} + 4.5MO + 3SiO_{2} + 4H_{2}O + 0.083O_{2} \rightarrow 0.167M_{3}O_{4} + M_{5}AlSi_{3}AlO_{10}(OH)_{8}$$
 (Reaction 1)

where M stands for Cr, Fe^{3+} , Fe^{2+} and Mg in spinels, as well as Fe^{2+} and Mg in the fluid and chlorite. It is likely in such a reaction that the fluid was derived from the adjacent peridotites. We emphasize that oxidation of Fe^{2+} to Fe^{3+} rather than diffusion of Fe^{2+} from olivine to Cr-spinel aided lamellae-rich spinel growth.

Phase relations for massive chromitites support that Cr-spinel reacts with olivine to produce porous spinel according to the reaction proposed by [86]:

$$\begin{array}{l} 4(Mg_{0.7}Fe_{0.3})CrAlO_4 + 4(Mg_{1.88}Fe_{0.12})SiO_4 + 2SiO_{2aq} + 8H_2O \rightarrow \\ 2(Mg_{4.61}Fe_{0.31})AlSi_3AlO_{10}(OH)_8 + 2(Mg_{0.55}Fe_{0.45})Cr_2O_4 \end{array}$$
(Reaction 2)

Reaction (2) considers only Mg end-members and proceeds under reducing conditions. A similar reaction can explain porous spinel for lamellae-rich spinel substitution with the reactant spinel having higher Cr/Al ratio and Fe³⁺ abundance compared to the one used in Reaction (2). The thickness of the chlorite zones produced by Reaction (1) (separating lamellae-rich spinel from olivine,) is not enough to prevent Reaction (2) but once a thin porous rim will form Reaction (2) will stop because the reactants will be isolated from each other. The conversion of lamellae-rich spinel to porous spinel is marked by an increase in the Fe²⁺ content of the latter plausibly due to the combined effect of Fe³⁺ reduction owing to: (i) interaction with a reducing fluid and (/or) (ii) the simultaneous breakdown of the serpentine proportion of the Mg-silicate needles in lamellae-rich spinel (as confirmed by average SEM/EDS data), following the very general scheme:

*a*lamellae-rich spinel + *b*Serpentine
$$\rightarrow$$
 *c*Porous spinel + *d*Clinochlore (Reaction 3)

where *a*, *b*, *c* and *d* stand for the appropriate integers.

Phase relations in the system $(Fe^{2+},Mg)Cr_2O_4-(Fe^{2+},Mg)Fe^{3+}_2O_4-(Fe^{2+},Mg)Al_2O_4$ [88] suggest that porous rims started forming at slightly higher *T* compared to the lamellae-rich ones (Figure 17). The documented overgrowth of porous rims onto the lamellae-rich zones implies an abrupt change of conditions from oxidizing to reducing. The extremely thin nature of these alteration rims suggests that they formed at a low fluid/chromitite ratio; a greater abundance of porous spinel indicates that the second event was more widespread. We also note that altered Cr-spinel grains were not recognized in all samples, but were most abundant in the sheared (cataclastic) material. Chromian spinel displaying both types of texture was recognized in samples from the subcordant lenticular ore body. We conclude that the metamorphic processes did not operate uniformly; though, were probably controlled by shear deformation.



Figure 17. Compositional changes in spinel phases from the examined chromitites expressed in a triangular Al-Fe³⁺-Cr diagram with special reference to the fields of the different metamorphic facies defined for Cr-spinels by [89–91]. Solvus determined at 600, 550 and 500 °C by [88] for Cr-spinel coexisting with forsteritic olivine (Fo₉₀). Explanation of symbols as in Figure 11.

7.2.2. Zircon Re-Equilibration with Deuteric Fluids

The zircons of Ayios Stefanos were pseudomorphically replaced by Ca-bearing Zr-rich silicate minerals as a result of dissolution-reprecipitation processes [92,93] under reducing conditions prevailing during the post-magmatic stage of evolution. The replacing minerals are commonly mottled in appearance, and porous due to pristine zircon volume decrease (e.g., [39]). The sharp boundaries between the altered and intact areas in the partly replaced zircons (Figure 7b,c) correspond to the stage at which the advancing chemical front stopped. Zircon degradation to armstrongite is best described by the following reaction:

$$ZrSiO_4 + CaCO_3 + 5(H_4SiO_4)_{aq} \leftrightarrow CaZrSi_6O_{15} \cdot 3H_2O + 7H_2O + CO_2$$
(Reaction 4)

showing that the ingressing fluid had an acidic character [94]. Calciocatapleiite forms in undersaturated-in-H₄SiO₄ and Ca-bearing settings [95]. Both of these secondary, Ca-bearing Zr-rich silicate phases stabilize at crustal levels (<2.5 km) and *T* lower than 600 °C [96]. We suggest that zircons were compositionally altered in variable degrees by highly alkaline and Ca-rich fluids released during the serpentinization of peridotites-chromitites [73] or the tremolitization of clinopyroxene in the gabbroic intrusions (Unpubl. data). Another potential origin for these fluids is that they might represent remnant Ca-rich fluids left after the crystallization of zircons in the chromitites (causing auto-metasomatism).

The detection of non-formula compounds (CaO, Al_2O_3 , FeO) in most of the examined zircons (Table A4) can be explained by: (i) the presence of micro-inclusions or (ii) the incorporation of solvent substances in zircon through a diffusion-reaction process at *T* above 200 °C [97]. All zircons are free of visible inclusions; hence, the second explanation seems to be more valid. The common discovery of armstrongite pseudomorphs after zircon displaying surface pitting and a spongy internal texture is also in favor of zircon in situ alteration by hydrothermal processes.

Equilibration of zircon with aqueous fluids may be facilitated if the zircon is structurally damaged. Our data show that zircons experienced metamictization. This process is known for drastically quenching the CL emission and resetting the U-Pb system [39]. We note that the time difference between oceanic crust formation and emplacement is short for the neighboring Vourinos and Pindos ophiolites [98]. If the same scenario is applicable for Othris, then the time interval between gabbro intrusion in the chromitites and metamorphism/serpentinization should also be limited. So, it is likely that the examined zircons were modified first and then underwent serpentinization-related metamictization, possibly in fluid-assisted conditions (e.g., [82]).

7.3. Synthesis and Geochronological Implications

Both micro-textural and compositional characteristics of the Ayios Stefanos zircons indicate that they were introduced into the chromitites via a network of high-*T* fluids emanating from the gabbroic dykes that were syn-kinematically emplaced into the thrust (contact) zone between ultramafic mantle nappes. The ages of these zircons should mostly indicate the time of intrusion of their protolith, and that of incipient obduction rather than the time of mantle-hosted chromitite genesis. In the absence of isotopic data it is hard to reach a conclusion about the exact age of the gabbroic intrusions. We can, however, use our data to constrain the relative sequence of magmatic, tectonic and post-magmatic events in the study area. The common occurrence of deformed chromitites along the plagioclase-bearing lherzolite-harzburgite nappe contact implies that the latter served as a potential 'structural trap' for the ore bodies [33]. The intrusion of gabbroic dykes, showing a tectonic pattern in agreement with that of the deformation in the tectonically thinning zone, within the chromitites quite obviously illustrates that the formation of the ore bodies predated the intrusion of gabbros. The exact role of focused constrictive deformation in Cr-spinel metamorphic alteration is not yet completely understood; it could be envisaged that the thrust zone also served as a localized permeability path enabling the passage of post-magmatic fluids that modified Cr-spinel texture and composition during

ophiolite obduction. Petrographic observations (i.e., serpentine cutting clinochlore) document that serpentinization (and rodingitization) occurred after Cr-spinel post-magmatic modification, and were related to oceanic alteration that commonly accompanies ophiolite emplacement.

If the above geochronological assumptions are correct, then dating of the Ayios Stefanos zircons may serve as a potential way to date the initial stages of obduction in Othris as the ophiolitic slab was coming off the ridgecrest.

8. Concluding Remarks

The present study has led to the following conclusions:

- 1. The Ayios Stefanos Al-rich chromitites precipitated from an alkali-rich melt of medium-Ti basalt (MTB) affinity produced at a near-transform boundary of a slow-spreading ridge.
- 2. A few samples show limited Cr-spinel replacement by spinel with oriented lamellae of Mg-silicates (predominantly chlorite) ascribed to the infiltration of oxidizing fluids in the chromitites. Most specimens display common porous spinel for Cr-spinel substitution linked to Cr-spinel (or lamellae-rich spinel) breakdown after reaction with olivine in a reducing environment.
- 3. Chromitites host numerous tiny, subhedral to anhedral and elongated Zr-bearing silicate phase that are commonly placed in open and restored fractures in Cr-spinel. Textural associations and compositional data echo the possibility that zircons originate from high-*T* fluids emanating from the gabbroic dykes that intrude both chromitites and peridotites in the study area.
- 4. Zircon pseudomorphic replacement by Ca-bearing Zr-rich silicates and enrichment in solvent cation oxides (CaO, Al₂O₃ and FeO) provide evidence for zircon re-equilibration with deuteric fluids.
- 5. This study highlights that a clear understanding of the origin of zircons in ophiolitic chromitites is essential for the interpretation of the sequence of synchronological petrologic and deformation events recorded by upper-mantle rocks, including their obduction, emplacement and subsequent alteration.

Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/6/4/124/s1, Table S1: Pristine chromian spinel analyses, Table S2: Altered spinel analyses, Table S3: Zr-bearing silicate mineral analyses.

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Appendix A

Table A1. Summary of the main petrographic characteristics of the studied chromitites. Abbreviations: Cal = calcite; Chl = chlorite; Hgr = hydrogrossular; Ser = serpentine; Spn = Spinel; Tr = tremolite; Wo = wollastonite. The symbols: + and -, denote the accessory presence and absence of zircon, respectively.

Sample Number	Morphology	Chr Texture	Groundmass Texture	Secondary Phases	Zr-Si Phases	Other Features
1a	Boulder	Massive	Mesh	Srp, Chl, Tr, Hgr, Porous Spn	+	Hgr microveins
1b	Boulder	Massive	Interpenetrating	Srp, Chl, Tr, Porous Spn	+	Chr brecciation
2a	Boulder	Massive	Interlocking, bastite	Srp, Chl, Tr, Wo, Hgr	-	-
2b	Boulder	Massive	Interpenetrating, bastite	Srp, Chl, Wo	-	-
3a	Boulder	Massive	Mesh	Srp, Chl	-	Pull apart texture in Chr
3b	Boulder	Massive	Mesh	Srp, Chl, Hgr	-	Pull apart texture in Chr
3c	Boulder	Massive	Interpenetrating	Srp, Chl, Hgr	-	Microfolds
3d	Boulder	Massive	Interpenetrating	Srp, Chl, Hgr, Cal	-	Hgr-Cal intergrowths
4a	Boulder	Massive	Mesh	Srp, Chl, Wo	-	Lobate Chr
4b	Boulder	Semi-massive	Mesh	Srp, Chl	-	Pull apart texture in Chr
5	Boulder	Massive	Interpenetrating	Srp, Chl, Porous Spn	-	Chr brecciation
6	Boulder	Semi-massive	Mesh, bastite	Srp, Chl, Tr, Wo	+	Rt exsolutions
7a	Lenticular	Semi-massive	Interpenetrating, hourglass	Srp, Chl, Tr, Porous & Lamellae-rich Spn	-	Lobate Chr
7b	Lenticular	Massive	Interpenetrating, hourglass	Srp, Chl, Tr, Porous & Lamellae-rich Spn	-	Chl intersection by Srp
7c	Lenticular	Massive	Interpenetrating, mesh	Srp, Chl, Tr, Porous Spn	+	Chr brecciation
8	Lenticular	Semi-massive	Interpenetrating, mesh	Srp, Chl, Tr, Porous Spn	+	-

Sample/Analysis Number	SiO ₂ (wt %)	TiO ₂	Al_2O_3	Cr_2O_3	V_2O_3	FeO ^t	Fe ₂ O ₃ (rec.)	MnO	MgO	NiO	CaO	ZnO	Total
1-a/1	bdl	0.05	26.31	43.61	0.17	13.28	1.28	0.20	15.27	0.20	bdl	0.10	99.17
2-a/5	bdl	bdl	24.79	46.00	0.18	14.16	0.68	0.20	14.42	0.11	bdl	0.06	99.92
2-d/5	bdl	0.10	24.96	46.29	0.15	14.46	0.58	0.21	14.28	0.16	bdl	0.10	100.71
3-c/17	bdl	0.08	26.45	43.03	0.20	15.05	2.14	0.24	14.62	0.09	0.41	bdl	100.16
3-d/3	bdl	bdl	26.42	43.35	0.16	14.22	2.15	0.18	15.38	0.17	bdl	0.14	100.01
4-b/10	bdl	0.13	19.66	50.06	0.16	15.81	1.22	0.18	13.00	0.11	bdl	bdl	99.08
5/4	bdl	bdl	23.77	44.89	0.21	14.70	3.01	0.15	15.21	0.16	bdl	bdl	99.08
6/1	bdl	0.29	18.38	43.47	0.26	27.87	8.32	0.25	9.37	0.10	bdl	0.07	100.07
7-a/20	bdl	0.10	26.47	43.58	0.14	14.89	2.37	0.13	15.35	0.12	bdl	0.07	100.86
7-b/1	bdl	0.08	25.49	44.33	0.17	13.07	3.17	0.14	16.82	0.08	bdl	bdl	100.18
7-c/3	bdl	0.07	24.96	45.99	0.13	12.89	1.14	0.16	15.57	0.11	bdl	bdl	99.90
8/9	0.03	0.16	17.60	50.91	0.21	16.62	4.52	0.38	14.41	na	bdl	0.08	100.39
Apfu	Si	Ti	Al	Cr	\mathbf{V}	Fe ³⁺	Fe ²⁺	Mn	Mg	Ni	Ca	Zn	Total
1-a/1	-	-	0.93	1.04	-	0.03	0.31	0.01	0.68	0.01	-	-	3.01
2-a/5	-	-	0.88	1.10	-	0.02	0.34	0.01	0.65	-	-	-	3.00
2-d/5	-	-	0.88	1.10	-	0.01	0.35	0.01	0.64	-	-	-	2.99
3-c/17	-	-	0.93	1.02	0.01	0.05	0.33	0.01	0.65	-	0.01	-	3.01
3-d/3	-	-	0.93	1.02	-	0.05	0.31	-	0.68	-	-	-	2.99
4-b/10	-	-	0.73	1.24	-	0.03	0.39	0.01	0.61	-	-	-	3.01
5/4	-	-	0.85	1.08	0.01	0.07	0.30	-	0.69	-	-	-	3.00
6/1	-	0.01	0.69	1.10	0.01	0.20	0.54	0.01	0.45	-	-	-	3.01
7-a/20	-	-	0.92	1.02	-	0.05	0.32	-	0.68	-	-	-	2.99
7-b/1	-	-	0.89	1.04	-	0.07	0.25	-	0.74	-	-	-	2.99
7-c/3	-	-	0.88	1.09	-	0.03	0.30	-	0.70	-	-	-	3.00
8/9	-	-	0.64	1.24	0.01	0.11	0.32	0.01	0.66	-	-	-	2.99

Table A2. Electron-microprobe analyses and structural formulae (on the basis of 4 atoms of O) of Cr-spinel. $Fe_2O_{3(rec.)}$ is not included in the Total of each analysis. Abbreviations: bdl = below detection limit; na = not analyzed.

Sample/Analysis Number	SiO ₂ (wt %)	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	V_2O_3	FeO	Fe ₂ O ₃ (rec.)	MnO	MgO	NiO	CaO	ZnO	Total
1-a/6	bdl	0.16	17.25	50.67	0.13	18.35	3.20	0.20	12.32	0.06	bdl	bdl	99.14
1-b/6	bdl	0.10	17.36	51.11	0.19	17.11	3.97	0.31	13.69	na	bdl	0.06	99.93
1-b/8	bdl	0.11	15.91	51.68	0.18	18.42	5.08	0.36	13.37	na	bdl	bdl	100.03
5/17	bdl	0.12	18.30	49.63	0.17	18.74	2.51	0.33	11.52	0.10	bdl	0.21	99.12
7-a/7	0.56	0.11	8.57	48.38	0.17	21.35	15.52	0.18	16.11	0.09	bdl	bdl	95.52
7-a/8	bdl	0.11	14.32	48.52	0.20	24.14	10.19	0.20	12.56	0.20	bdl	bdl	100.25
7-b/2	0.61	bdl	12.57	45.63	0.14	16.63	12.67	0.22	17.37	0.03	0.04	0.10	93.34
7-b/3	0.01	0.06	12.04	49.12	0.14	25.83	12.08	0.24	12.17	0.19	bdl	0.19	99.99
7-b/21	8.30	bdl	8.98	45.52	0.10	18.13	11.81	0.18	17.04	0.09	bdl	bdl	98.34
7-b/22	0.06	0.07	0.55	56.11	0.21	29.38	16.68	0.26	11.19	bdl	bdl	bdl	97.83
7-c/2	0.06	0.10	7.80	60.48	0.20	20.74	3.45	0.31	9.97	0.11	bdl	bdl	99.77
7-c/4	bdl	0.06	8.36	58.96	0.21	22.61	3.72	0.30	8.89	0.14	bdl	bdl	99.53
8/6	bdl	0.54	8.27	54.43	0.26	23.20	9.70	0.49	11.94	na	0.03	bdl	99.16
Apfu	Si	Ti	Al	Cr	\mathbf{V}	Fe ³⁺	Fe ²⁺	Mn	Mg	Ni	Ca	Zn	Total
1-a/6	-	-	0.65	1.27	-	0.08	0.41	0.01	0.58	-	-	-	3.00
1-b/6	-	-	0.64	1.26	0.01	0.09	0.35	0.01	0.64	-	-	-	3.00
1-b/8	-	-	0.59	1.28	0.01	0.12	0.36	0.01	0.63	-	-	-	3.00
5/17	-	-	0.69	1.25	-	0.06	0.44	0.01	0.55	-	-	0.01	3.01
7-a/7	0.02	-	0.33	1.26	0.01	0.38	0.20	0.01	0.79	-	-	-	3.00
7-a/8	-	-	0.54	1.22	0.01	0.24	0.40	0.01	0.59	0.01	-	-	3.02
7-b/2	0.02	-	0.48	1.18	-	0.31	0.14	0.01	0.85	-	-	-	2.99
7-b/3	-	-	0.46	1.25	-	0.29	0.40	0.01	0.58	0.01	-	0.01	3.01
7-b/21	0.26	-	0.33	1.13	-	0.28	0.20	0.01	0.80	-	-	-	3.01
7-b/22	-	-	0.02	1.53	0.01	0.43	0.42	0.01	0.58	-	-	-	3.00
7-c/2	-	-	0.31	1.60	0.01	0.09	0.49	0.01	0.50	-	-	-	3.01
7-c/4	-	-	0.33	1.57	0.01	0.09	0.54	0.01	0.45	-	-	-	3.00
8/6	-	0.01	0.32	1.42	0.01	0.24	0.40	0.01	0.59	-	-	-	3.00

Table A3. Electron-microprobe analyses and structural formulae (on the basis of 4 atoms of O) of porous spinel and lamellae-rich spinel. All analyses correspond to porous spinel except for analyses 7-a/7, 7-b/2 and 7-b/21, which represent lamellae-rich spinel. Analyses from samples 7-a and 7-b represent pair analyses. Fe₂O_{3(rec.)} is not included in the Total of each analysis. Abbreviations: bdl = below detection limit; na = not analyzed.

Table A4. Electron-microprobe analyses of Zr-bearing silicate phases from the studied chromitites. All analyses correspond to zircon except for 40 and 41 which represent calciocatapleiite and armstrongite, respectively. Structural formulae for zircon were calculated on the basis of 4 atoms of O, whereas those of calciocatapleiite and armstrongite were calculated on the basis of 9 and 15 atoms of O. Analyses 35–37 correspond to zircon texturally associated with porous spinel and chlorite. The full range of detected major oxides for analyses 40 and 41 is given in the Supplementary files. Abbreviations: An. = analysis number; D.L. = detection limit; bdl = below detection limit.

An.	SiO ₂ (wt %)	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	Y_2O_3	ZrO ₂	Ce ₂ O ₃	HfO ₂	UO ₂	ThO ₂	P ₂ O ₅	Total
4	35.63	0.12	bdl	bdl	0.05	0.02	0.98	62.63	bdl	bdl	0.06	bdl	bdl	99.49
5	35.66	1.25	bdl	0.29	2.06	0.05	0.86	59.53	bdl	0.33	bdl	0.26	bdl	100.29
6	37.14	0.86	bdl	0.24	0.82	bdl	0.92	60.24	bdl	bdl	0.12	0.15	bdl	100.49
12	36.00	0.51	bdl	0.15	0.32	0.02	1.16	61.08	bdl	0.00	0.16	bdl	bdl	99.40
13	36.57	0.65	bdl	0.30	0.67	0.04	0.86	59.12	0.12	0.28	0.11	bdl	bdl	98.72
16	36.54	0.19	bdl	0.20	0.20	0.07	0.53	63.05	bdl	bdl	bdl	bdl	bdl	100.78
21	36.41	0.40	bdl	0.08	0.00	0.04	0.71	61.77	bdl	0.39	0.06	0.09	bdl	99.95
23	37.62	1.12	bdl	0.32	0.17	0.00	0.63	58.07	bdl	0.20	bdl	0.08	bdl	98.21
25	36.15	0.16	bdl	0.09	0.06	0.00	0.44	62.70	bdl	0.41	bdl	bdl	bdl	100.01
35	35.97	0.14	1.27	3.62	0.21	0.03	0.07	52.71	0.08	1.73	0.15	bdl	0.07	96.05
36	34.28	bdl	0.32	0.03	0.07	0.03	0.13	63.25	0.15	1.68	bdl	bdl	0.36	100.30
37	34.17	bdl	0.37	0.05	0.04	bdl	0.19	64.03	0.09	1.53	bdl	bdl	0.43	100.90
40	45.88	0.19	2.18	3.74	14.58	0.04	0.42	22.36	0.09	1.03	0.21	0.08	0.15	90.95
41	48.86	0.15	1.60	3.60	7.95	0.05	0.47	25.79	0.00	0.89	0.08	0.21	0.10	89.75
Apfu	Si	A1	Fe ²⁺	Mg	Ca	Na	Ŷ	7.r	Ce	Hf	U	Th	р	Total
1				0			-				U	111	1	Iotai
4	1.07		-		-	-	0.02	0.92	-	-	-	-	-	2.01
4 5	1.07 1.06	- 0.04	-	- 0.01	- 0.07	-	0.02 0.01	0.92 0.86		-		-	-	2.01 2.05
4 5 6	1.07 1.06 1.09	- 0.04 0.03		- 0.01 0.01	- 0.07 0.03		0.02 0.01 0.01	0.92 0.86 0.86						2.01 2.05 2.03
4 5 6 12	1.07 1.06 1.09 1.07	- 0.04 0.03 0.02	- - - -	- 0.01 0.01 0.01	- 0.07 0.03 0.01		0.02 0.01 0.01 0.02	0.92 0.86 0.86 0.89						2.01 2.05 2.03 2.02
4 5 6 12 13	1.07 1.06 1.09 1.07 1.09	0.04 0.03 0.02 0.02	- - - -	- 0.01 0.01 0.01 0.01	- 0.07 0.03 0.01 0.02		0.02 0.01 0.01 0.02 0.01	0.92 0.86 0.86 0.89 0.86	- - - - -	 - - - -	- - - - -			2.01 2.05 2.03 2.02 2.01
4 5 6 12 13 16	1.07 1.06 1.09 1.07 1.09 1.08	- 0.04 0.03 0.02 0.02 0.02 0.01	- - - - -	- 0.01 0.01 0.01 0.01 0.01 0.01	- 0.07 0.03 0.01 0.02 0.01	- - - - - -	0.02 0.01 0.01 0.02 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91	- - - - - -			- - - - -		2.01 2.05 2.03 2.02 2.01 2.03
4 5 6 12 13 16 21	1.07 1.06 1.09 1.07 1.09 1.08 1.08	- 0.04 0.03 0.02 0.02 0.01 0.01		- 0.01 0.01 0.01 0.01 0.01 -	0.07 0.03 0.01 0.02 0.01	- - - - - - -	0.02 0.01 0.01 0.02 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89	- - - - - - - - -		- - - - - - -			2.01 2.05 2.03 2.02 2.01 2.03 1.99
4 5 6 12 13 16 21 23	$ 1.07 \\ 1.06 \\ 1.09 \\ 1.07 \\ 1.09 \\ 1.08 \\ 1.08 \\ 1.08 \\ 1.11 $	- 0.04 0.03 0.02 0.02 0.01 0.01 0.01 0.04	- - - - - - - -	- 0.01 0.01 0.01 0.01 0.01 - 0.01	- 0.07 0.03 0.01 0.02 0.01 - 0.01		0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89 0.84	- - - - - - - - -		- - - - - - - - - -			2.01 2.05 2.03 2.02 2.01 2.03 1.99 2.02
4 5 6 12 13 16 21 23 25	$ 1.07 \\ 1.06 \\ 1.09 \\ 1.07 \\ 1.09 \\ 1.08 \\ 1.08 \\ 1.11 \\ 1.08 $	- 0.04 0.03 0.02 0.02 0.01 0.01 0.04 0.01	- - - - - - - - -	- 0.01 0.01 0.01 0.01 - 0.01 -	- 0.07 0.03 0.01 0.02 0.01 - 0.01		0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89 0.84 0.91	- - - - - - - - -		- - - - - - - - -			2.01 2.05 2.03 2.02 2.01 2.03 1.99 2.02 2.01
4 5 6 12 13 16 21 23 25 35	$ \begin{array}{r} 1.07\\ 1.06\\ 1.09\\ 1.07\\ 1.09\\ 1.08\\ 1.08\\ 1.11\\ 1.08\\ 1.09\\ \end{array} $	0.04 0.03 0.02 0.02 0.01 0.01 0.04 0.01 0.01	- - - - - - - - - - - - 0.03	- 0.01 0.01 0.01 0.01 - 0.01 - 0.01	- 0.07 0.03 0.01 0.02 0.01 - 0.01		0.02 0.01 0.01 0.02 0.01 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89 0.84 0.91 0.78	- - - - - - - - - - -					2.01 2.05 2.03 2.02 2.01 2.03 1.99 2.02 2.01 2.09
4 5 6 12 13 16 21 23 25 35 36	$ \begin{array}{c} 1.07\\ 1.06\\ 1.09\\ 1.07\\ 1.09\\ 1.08\\ 1.08\\ 1.11\\ 1.08\\ 1.09\\ 1.09\\ 1.03\\ \end{array} $	0.04 0.03 0.02 0.01 0.01 0.01 0.04 0.01 0.01	- - - - - - - - - - - - - - - - - - -	- 0.01 0.01 0.01 0.01 - 0.01 - 0.16 -	- 0.07 0.03 0.01 0.02 0.01 - 0.01 - 0.01		0.02 0.01 0.01 0.02 0.01 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89 0.84 0.91 0.78 0.93	- - - - - - - - - - - -				- - - - - - - - - - 0.01	2.01 2.05 2.03 2.02 2.01 2.03 1.99 2.02 2.01 2.09 1.99
4 5 6 12 13 16 21 23 25 35 36 37	$\begin{array}{c} 1.07\\ 1.06\\ 1.09\\ 1.07\\ 1.09\\ 1.08\\ 1.08\\ 1.08\\ 1.11\\ 1.08\\ 1.09\\ 1.03\\ 1.03\\ 1.03\end{array}$	0.04 0.03 0.02 0.01 0.01 0.01 0.04 0.01 0.01 - -	- - - - - - - - - - - - - - - - - - -	- 0.01 0.01 0.01 0.01 - 0.01 - 0.16 - -	0.07 0.03 0.01 0.02 0.01 - 0.01 - 0.01 - -		0.02 0.01 0.01 0.02 0.01 0.01 0.01 0.01	0.92 0.86 0.86 0.89 0.86 0.91 0.89 0.84 0.91 0.78 0.93 0.94	- - - - - - - - - - - - - -		- - - - - - - - - - - - - -		- - - - - - - - - - - - 0.01 0.01	2.01 2.05 2.03 2.02 2.01 2.03 1.99 2.02 2.01 2.09 1.99 2.00
4 5 6 12 13 16 21 23 25 35 36 37 40	$\begin{array}{c} 1.07\\ 1.06\\ 1.09\\ 1.07\\ 1.09\\ 1.08\\ 1.08\\ 1.08\\ 1.11\\ 1.08\\ 1.09\\ 1.03\\ 1.03\\ 2.98\end{array}$	0.04 0.03 0.02 0.02 0.01 0.01 0.04 0.01 0.01 - 0.01	- - - - - - - - - - - - - - - - - - -		- 0.07 0.03 0.01 0.02 0.01 - 0.01 - 0.01 - 1.02		0.02 0.01 0.01 0.02 0.01 0.01 0.01 0.01	0.92 0.86 0.89 0.86 0.91 0.89 0.84 0.91 0.78 0.93 0.94 0.71	- - - - - - - - - - - - - - -	- - - - - - - - - - - - 0.01 0.01 0.01 0	- - - - - - - - - - - - - - -		- - - - - - - - - - - 0.01 0.01 0.01	$\begin{array}{c} 2.01\\ 2.05\\ 2.03\\ 2.02\\ 2.01\\ 2.03\\ 1.99\\ 2.02\\ 2.01\\ 2.09\\ 1.99\\ 2.00\\ 5.24 \end{array}$

Raman Analysis Number	Eg (Te	trahedron I	Rotation)	A _{1g} (Sym	metric Ben	ding, v_2)	B_{1g} (Antisym. Stetching, v_3)			
Kaman Anarysis Number	v	FWHM	Ι	v	FWHM	I	v	FWHM	Ι	
15.12.078	353.4	12.40	319.50	438.90	8.06	257.75	1003.7	10.09	373.74	
15.12.080	352.1	17.17	531.07	438.05	19.38	735.50	1002.7	11.30	417.48	
15.12.084	354.1	10.11	475.50	438.60	13.80	989.50	1005.1	10.90	816.26	
15.12.087	353.4	12.70	381.29	438.99	16.16	780.10	1003.7	11.90	624.87	
15.12.091	353.1	14.70	198.52	438.96	14.86	504.21	1003.6	12.10	310.05	
15.12.096	353.9	12.80	202.29	438.67	14.14	454.63	1003.7	12.60	315.24	
15.12.099	355.4	11.30	402.32	438.78	15.38	809.33	1003.9	13.34	738.46	
15.12.102	355.2	16.08	1535.80	439.27	16.44	787.89	1004.3	13.60	694.56	
15.12.105	355.1	15.14	1927.50	439.56	15.52	976.13	1004.9	13.32	935.55	
15.12.110	353.4	12.34	436.40	439.24	13.42	1210.50	1004.1	14.54	1098.04	
15.12.117	353.5	13.54	779.04	438.25	15.78	766.12	1004.5	13.08	700.00	
15.12.126	354.8	9.80	151.80	439.40	14.86	599.60	1005.6	14.86	249.70	

Table A5. Parameters of the Raman bands of representative zircon grains from the studied chromitites, where v is in cm^{-1} and *I* is in counts.

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