Fully oxidized chromite in the Serra Alta (South Portugal) quartzites: chemical and structural characterization and geological implications

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Abstract

Several quartzite bodies outcrop along the Ferreira-Ficalho Thrust Fault (South Portugal), a major accident of the Iberian Variscan Orogen. The sediment is a very pure quartz sandstone, with trace amounts of ultra-resistant heavy minerals and chromite. Chemical characterization (microprobe analyses and Mössbauer spectroscopy) showed the chromite to be unique: besides being Zn-rich, complexly zoned and a cation deficient spinel, all the iron was found to be fully oxidized to Fe^{3+}. Structure refinement of single-crystal X-ray diffraction intensities unambiguously identifies the mineral as a chromite and the Mössbauer data are consistent with tetrahedrally coordinated Fe^{3+} in the spinel structure. Current geodynamical models see the Ferreira-Ficalho Thrust Fault as a first-order suture resulting from a complex collision of two distinct continental blocks with partial obduction of the intervening oceanic crust. The chromite grains could be envisaged as remnants of an early erosion of this obducted oceanic crust, but its unique chemical character does not allow any definite conclusion. Yet, the complete quartzite heavy mineral contents and its petrographic features are not consistent with their deposition within a continental collision situation.

KEYWORDS: chromite, quartzite, oxidation, Serra Alta, Portugal.

Introduction

THE introduction and widespread use of the electron microprobe in the investigation of the chemical composition of minerals is gradually showing that zinc is a fairly common element in chromian spinels. This feature, although not so rare as formerly believed, is still considered worth reporting wherever it is found, for the geological context where zincian chromites occur indicates unusual alteration conditions. The works of Groves et al. (1977) and Liipo et al. (1995) are among the very few where Zn incorporation in chromian spinels is claimed to be a magmatic stage inheritance.

Bernier (1990) shows that, in most cases, zincian-chromian spinels are associated to sulphide miner-alizations, those zincian spinels that do occur in unmineralized rocks having a generally much lower Zn content than those associated to mineralizations. The discussion of Bernier (1990) also shows that metamorphism is not considered to be an important factor in the primary incorporation of zinc, though its effects are visible in the development of complex zonation patterns inside the spinel crystals.

In the present work, the study of a chromian spinel, occurring as sparse detrital grains in Devonian quartzites of southern Portugal, is emphasized because of its unusual chemical composition and of the geological implications of its presence. The quartzites where chromite is found have not suffered any extensive metasomatic alteration (mineralizing or otherwise) but were metamorphosed in the

greenschist facies (Munhá, 1976) during the Variscan orogeny.

Geological setting

The quartzite outcrop at Serra Alta (a low ridge located some 70 km ESE of Lisbon, Fig. 1) is the northwesternmost of a series of lenticular quartzite bodies that occur at most at some hundreds of meters to the south of a major tectonic accident, the Ferreira-Ficalho thrust, separating the Ossa-Morena and the South Portuguese Zones of the Iberian Variscan Orogen. The South Portuguese Zone is composed mainly of marine sedimentary successions ranging from Upper Devonian to Middle Carboniferous and was the site of important Lower Carboniferous acid

(sometimes basic) volcanism associated to the giant massive sulphides ore deposits of the Iberian Pyrite Belt. The sedimentary rocks are lithologically quite monotonous, for most of the formations include essentially pelites or have a turbiditic character. In this zone the pre-Variscan sedimentation ended up with the deposition of a very thick turbiditic sequence, whose age decreases southwestwards across strike. This age gradient is a general feature of the South Portuguese Zone, since the scant palaeontological evidence available indicates that formations to the north are older than more southerly situated formations. Despite strong southward tectonic imbrication, this and the fact that the age of the main phase of deformation also decreases to the south, has fostered hypotheses considering the
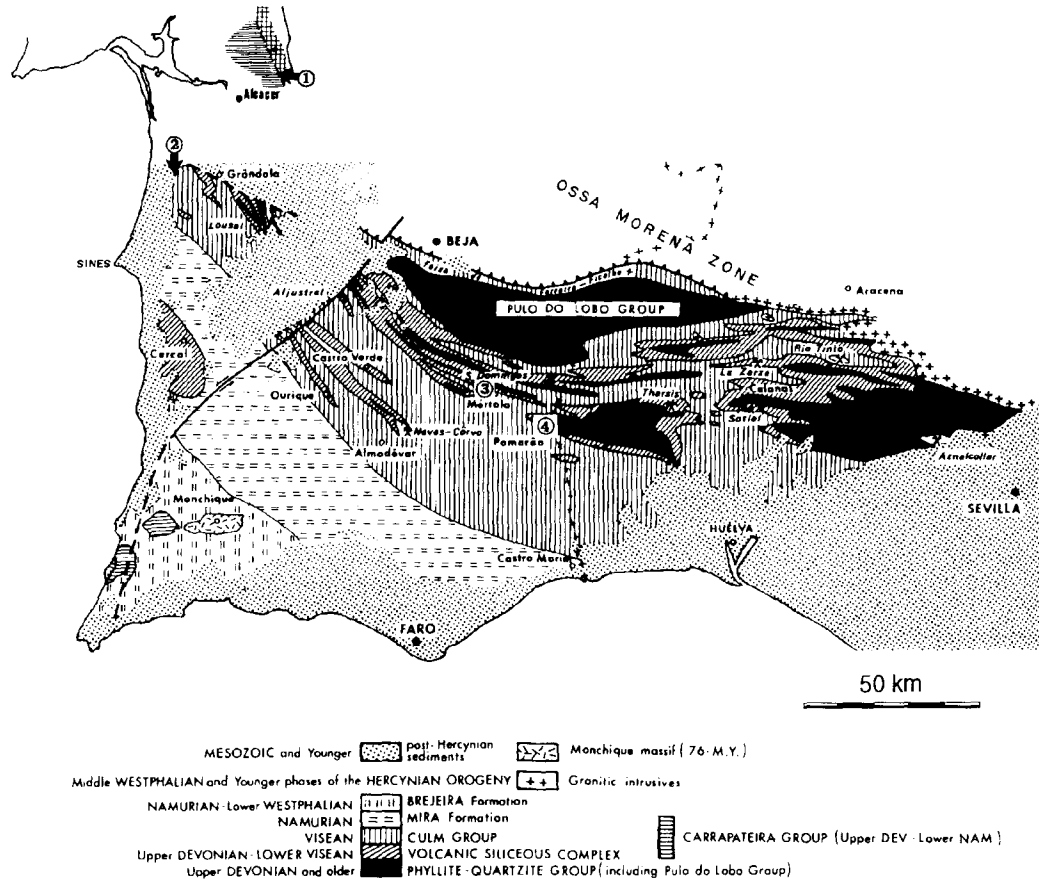

FIG. 1 Simplified geological map of the South Portuguese Zone. The Culm Group and the Mira and Brejeira Formations make up the Carbonifeous turbidite sequence referred to in the text. Numbers denote the localities where detrital chromite was found in quartzitic rocks: 1. Serra Alta; 2. Melides; 3. Cela; 4. Pomarão. Adapted from Dallmeyer and Martínez García (1990), pp. 365 and 370.

South Portuguese Zone sediments as originating from the erosion of what is now the Ossa-Morena Zone, lying to the north of the Ferreira-Ficalho thrust. Yet, direct evidence for this northward origin of the sediments has not been found since all rock and mineral fragments found in the sediments of the South Portuguese Zone are compatible with an intrabasinal origin and the very few instances of preserved sedimentary structures provide scant paleocurrent data, concentrated in turbiditic formations and indicating mostly along strike (i.e. parallel to the Ferreira-Ficalho thrust) currents.

The Ossa-Morena Zone differs from the South Portuguese Zone in that it includes the presence of rocks ascribed to all ages from an unspecified Precambrian up to Upper Carboniferous, of a thick carbonate platform of Georgian age, of abundant igneous rocks and of two belts of high-grade metamorphism, one of which, oblique to the strike, is formed by a series of thermal domes associated with important magmatic activity (Ribeiro et al., 1979) and occurs near the Ferreira-Ficalho thrust. Deformation is intense and polyphasic (Fonseca, 1995), the vergence of the structures varying from phase to phase. In the vicinity of the Ferreira-Ficalho thrust, the first phase of deformation generated north vergent structures in the Ossa-Morena Zone, tentatively interpreted as correlative of the obduction of the very strongly deformed and dismembered Beja-Acebuches Ophiolite Complex, a set of scattered outcrops of ultrabasic and basic rocks of oceanic affinities occurring just north of the Ferreira-Ficalho thrust and representing a remain of a small Palaeozoic ocean basin situated between the Ossa-Morena and the South Portuguese Zones.

The Serra Alta quartzites are embedded in what is collectively known as "Formação da Horta da Torre" (Oliveira et al., 1986). It can be said that this formation name covers all the rocks immediately to the south of the Ferreira-Ficalho thrust: these are mostly pelites, often with a turbiditic character shown by a rhythmic layering of schists and greywackes displaying graded bedding and abundant lithoclasts (of acid and basic volcanic rocks; Schermerhorn, 1971) with some volcanic intercalations and the quartzites just referred to. Limestone lenses cited in the literature as occurring just south of the thrust or, sometimes, just north of it, are now believed (Fonseca, 1996, pers. comm.) to be simply a result of metasomatic deposition of carbonates caused by fluids circulating in the thrust plane.

The reason why the quartzites should outcrop only in the immediate vicinity of the thrust fault is not known, and causes difficult problems of interpretation. The best explanation available holds that the sands have accumulated ahead of the advancing thrust front as a result of its erosion, but it is not understood why the sands should be, as observed, sedimentologically so mature nor why the thrust plane should follow so closely the level of deposition of the sands resulting from the erosion of the moving higher block.

The Serra Alta quartzite is composed almost exclusively of quartz. The grains are quite coarse and can be seen to have been rounded in the few instances where their original sedimentary form is still preserved. Apart from a few small laths of muscovite there are no minerals that could be the metamorphic equivalent of a clayey matrix. There has been intense deposition of silica, welding together the original grains. Deformation is high: evidence for internal deformation of quartz (expressed mainly by conspicuous wavy extinction, subgrains and deformation bands) is ubiquitous and overwhelming; the individual grains were often severely sheared, having become elongated (aspect ratios in the vicinity of 1:2 are not rare), and sometimes, along narrow corridors visible in thin section, they were completely destroyed, having been replaced by a fine mass of recrystallized quartz.

Apart from quartz and rare muscovite, there are trace amounts of detrital heavy minerals. The most common one, representing more than 70% of the heavy mineral concentrate, is zircon, as non-metamict grains, very well sorted, very well rounded and colourless to pale pink. Rutile, as orange to yellow-brown prismatic grains is the next most abundant heavy mineral, followed by tourmaline as green to brown, rounded spheroidal or prismatic grains. Rare chromite, as rounded to irregular opaque grains, make up the rest of the suite. The heavy mineral grains are noticeably smaller than the grains of quartz, this being especially true of zircon and chromite. While the grains of quartz vary between 0.3 and 0.5 mm across (exact original dimensions are difficult to evaluate because of deformation), the heavy mineral grains have a much better calibration and diameters very near 0.1 mm. It should also be made clear that no mineral other than quartz is visibly deformed, this mineral having accommodated all the deformation, as is to be expected from the style of deformation and metamorphic grade.

At Serra Alta, a microprobe investigation was made of the detrital tourmaline chemical composition. The results (Figueiras and Barriga, 1991) indicate a very homogeneous population (many grains have almost identical chemical compositions) whose individual grains have crystallized in equilibrium with aluminium-saturated metamorphic rocks.

The Serra Alta quartzite is almost identical to those occurring in other places of the South Portuguese Zone. All are very pure quartzites and have trace amounts of the same heavy mineral suite

found at Serra Alta. The most important distinguishing feature of the Serra Alta quartzite is the presence of chromite in more than trace amounts in the heavy mineral concentrates, but the dominance of zircon, its fine, well-rounded and well-sorted character, and the presence of a very subordinate and chemically very homogeneous population of tourmaline grains are also worth mentioning.

Experimental

Heavy mineral separation and concentration

Since the heavy mineral contents of the Serra Alta quartzite is so low, simply crushing it and extracting whatever is denser than bromoform yields a concentrate overwhelmingly dominated by the iron oxides/hydroxides deposited by the Neogene pedogenic alteration. Moreover, crushing the rock to the fine sand size needed to liberate the heavy mineral grains from quartz would have obliterated the form of the grains, thus preventing the recognition of any neoformation crystal that might be present. Therefore, the rock was crushed to fine gravel-size fragments and treated with a 33% solution of HF until all quartz (along with the Neogene oxides/hydroxides) was dissolved. The residue was rinsed with distilled water and mounted and polished to a high degree of perfection for microscopic observation and electron microprobe analysis using the procedure described by Figueiras and Barriga (1990).

To ensure a 100% pure chromite concentrate for Mössbauer spectroscopy, chromite grains were hand-picked under the stereoscopic microscope from the heavy mineral concentrate, grains without pitch-black colour and shiny sub-metallic luster being rejected.

HF treatments are a common practice to obtain high purity spinel separates for Mössbauer spectroscopy studies (e.g. McGuire et al., 1991; Wood and Virgo, 1989). Nevertheless, due to the surprising results obtained for the Serra Alta chromite, a sample of the Thetford (Quebec, Canada) chromitite was studied in order to check if the HF treatment might change the oxidation state of iron in chromite, or otherwise alter its chemical composition: first, it was divided in two aliquots, one of which was treated according to the same procedure used on the Serra Alta quartzite, the second one having been crushed to the dimensions of fine sand (using a cylinder rock crusher), water-rinsed to get rid of dust, and magnetically liberated from steel particles contributed by the rock crusher; the different mineral phases of the resulting sand were then pre-separated using a Franz electromagnetic separator till a pre-concentrate of chromite was obtained which was hand-picked to achieve a 100% pure chromite concentrate. The

chromite of both aliquots was later investigated by Mössbauer spectroscopy.

Microprobe analysis

Microprobe analyses were conducted using a JEOL JCXA 733 microprobe. Analytical conditions were beam diameter reduced to a point (beam focused), accelerating voltage 18 kV, and current intensity 25 nA. Standardization was made using chromite for Cr, magnetite for Fe, spinel for Al and Mg, zinc and vanadium metals, rhodonite for Mn and ilmenite for Ti. Si, Ca, Na and K were sometimes analysed, using wollastonite (for Si and Ca), kaersutite and adularia as standards, respectively.

Single-crystal X-ray diffraction (XRD)

Four approximately equant grains (dimensions ranging from 0.07 up to 0.11 mm) selected from the Serra Alta chromite concentrate were glued on top of glass fibres and transferred to a goniometer head mounted on an Enraf Nonius CAD-4 diffractometer. All of them were found to crystallize in a cubic face-centred crystal structure with similar unit-cell parameters (in the range 8.200–8.206 Å). Diffracted X-ray intensities were collected at room temperature for one of the crystals using an ω-2θ scan mode and graphite monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å). This same grain was later mounted and polished by a process modified from Figueiras and Barriga (1990), so that good microprobe analyses could be obtained.

Mössbauer spectroscopy

Mössbauer spectra were measured in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi [57]Co source in a Rh matrix. The velocity scale was calibrated using an α-Fe foil at room temperature. Spectra were obtained at 300 K and 80 K. Low-temperature measurements were performed using a liquid-nitrogen flow cryostat.

Three Mössbauer absorbers were prepared: one from a suitable amount of the Serra Alta chromite grains and the remaining two from both aliquots of the Thetford chromite grains. The grains were powdered in an agate mortar and the absorbers were finally obtained by pressing the sample powder (5 mg of natural Fe/cm^2) into a perspex holder.

Mössbauer spectra were analysed using a modified version (Waerenborgh, et al. 1994a,b) of the non-linear least-squares computer method of Stone (1967), which allowed the fitting of quadrupole splitting distributions.

Results

Electron microprobe analysis

Table 1 is a sample of the chemical compositions obtained by electron microprobe analysis on the Serra Alta chromite grains.

Many of the analyses performed on chromite do not sum to 100%, even when recalculated (as in Table 1) according to the oxidation state of iron obtained by Mössbauer spectroscopy. The reasons for that could not be determined, for the presence of all elements within the reach of the microprobe was checked and the probe gave consistently good results when analysing standard chromites or chromites other than those of Serra Alta.

All grains investigated were found to vary compositionally from point to point. This chemical zonation is not detectable by optical means, and when observed with the electron probe, is shown to have no discernible pattern of variation from rim to core or in any specific direction, the measured concentrations of several elements varying erratically from one point to another. Under the scanning

electron microscope, the grains are sometimes seen to consist of a multitude of very thin (< 1 μm) zones that form erratic, curved or concentric patterns, several of the latter co-existing in each grain, centred about no special location.

Since these zonation patterns are not optically visible, it was not possible to position the microprobe electron beam in such a way as to obtain the composition of each zone separately. Moreover, the zones are too thin to allow proper analytical resolution. Therefore, the compositions shown in columns 3−9 of Table 1 must be considered as local averages, the exact point compositions, normally obtainable at the resolution scale of the electron microprobe, remaining unknown.

None of the analyses performed yielded the chemical composition of a stoichiometric spinel. Values of Cr + Al were found to be normal for this type of spinel, but there is a systematic, although variable, overall Fe + Mg + Zn cation deficiency. Inside each grain, the concentrations of Cr and Al are almost constant and the chemical variations observed are due to the behaviour of the remaining elements present. Iron shows low amplitude variations, some-

TABLE 1. Representative electron microprobe analytical results of the Serra Alta chromite grains

	1	2	3	4	5	6	7	8	9
SiO_2	0.31	0.13							
TiO_2	0.03	0.01	0.28	0.14	0.28	0.07	0.21	0.03	0.00
Al_2O_3	23.61	0.79	10.28	19.10	27.89	18.81	9.97	20.25	15.68
V_2O_3	0.10	0.03	0.13	0.23	0.18	0.18	0.19	0.31	0.12
Cr_2O_3	42.69	1.01	52.71	52.66	40.38	46.34	59.91	43.82	47.53
Fe_2O_3	21.93	1.12	33.62	15.99	21.07	13.32	21.86	18.98	13.46
MgO	2.64	1.40	1.83	10.05	7.43	3.27	1.97	0.08	0.04
MnO	0.28	0.04	0.39	0.36	0.40	0.39	0.57	0.39	0.41
FeO	0.40	0.02	0.62	0.29	0.39	0.24	0.40	0.35	0.25
ZnO	7.28	2.68	0.25	0.43	1.35	14.16	3.68	11.91	17.04
Total	99.30		100.11	99.25	99.37	96.78	98.76	96.12	94.53
Si	0.08	0.03							
Ti	0.01	0.00	0.05	0.03	0.05	0.01	0.04	0.01	0.00
Al	6.97	0.11	3.15	5.52	7.83	5.94	3.12	6.41	5.25
V	0.02	0.01	0.03	0.05	0.03	0.04	0.04	0.07	0.03
Cr	8.45	0.09	10.84	10.20	7.60	9.82	12.59	9.30	10.68
Fe^{3+}	4.13	0.20	6.58	2.95	3.78	2.69	4.37	3.84	2.88
Mg	0.99	0.50	0.71	3.67	2.64	1.31	0.78	0.03	0.02
Mn	0.06	0.01	0.09	0.07	0.08	0.09	0.13	0.09	0.10
Fe^{2+}	0.08	0.00	0.13	0.06	0.08	0.05	0.09	0.08	0.06
Zn	1.35	0.52	0.05	0.08	0.24	2.80	0.72	2.36	3.57
O	32		32	32	32	32	32	32	32

Column 1 is an average of 10 analyses performed on the grain which was subjected to single-crystal XRD and column 2 the corresponding standard deviations. Columns 3−9 are actual analyses performed on different grains. Fe_2O_3 and FeO calculated according to Mössbauer results.

times with well defined gradients in definite directions, but zinc and magnesium may show extreme and inversely correlated variations. This inverse correlation between Zn and Mg has previously been reported from other localities where metasomatic zincian chromites occur (e.g. Béziat and Monchoux, 1991, and Wylie *et al.*, 1987).
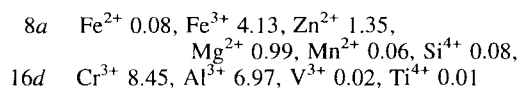
Since all chromite grains are composed of an indeterminable number of nanodomains with significantly different concentrations of Mg^{2+} and Zn^{2+}, an average chemical composition suitable for single-crystal XRD structure refinement had to be estimated. The chromite grain used for the single-crystal XRD data collection was polished until a plane passing approximately through its former center was exposed. Microprobe analyses were taken at several points of this plane and their arithmetic mean (Table 1, column 1) was taken as the best approximation of the average cation concentrations which contributed to the intensities of the X-ray beams diffracted by the whole single-crystal.

Single-crystal XRD and structure refinement

The unit-cell parameter *a* (Table 2) was obtained by least-squares refinement of the setting angles of 25 reflections with $28° < 2\theta < 60°$. The measured intensities were corrected for absorption by an empirical method based on ψ scans (North *et al.*, 1968) and for Lorentz-polarization effects (Fair, 1990).

The structure was refined by full-matrix least-squares based on the squares of the structure factors (Sheldrick, 1993). The scattering factor for O^{2-} was obtained from Hovestreydt (1983). For the other atoms, the scattering factors as well as the anomalous dispersion corrections were obtained from Ibers and Hamilton (1974). Scattering factors for fully ionized species were used in the final refinements because they always produced a slight improvement in the values of the agreement factors and negligible changes in the estimated values of the adjusted parameters. Space-group $Fd\bar{3}m$ was considered. Neither inconsistent equivalents nor systematic absence violations were observed. Extinction was found to be negligible.

As explained above the average chemical composition in column 1 of Table 1, and therefore full site occupancy of the 32*e* equiposition by O^{2-}, were assumed. The following cation site distribution was considered as a first approximation:

8*a* Fe^{2+} 0.08, Fe^{3+} 4.13, Zn^{2+} 1.35,
          Mg^{2+} 0.99, Mn^{2+} 0.06, Si^{4+} 0.08,
16*d* Cr^{3+} 8.45, Al^{3+} 6.97, V^{3+} 0.02, Ti^{4+} 0.01

Due to the large number of different cations, constraints on the cation distribution had to be imposed. Thus, assuming reasonable cation site preferences (O'Neill and Navrotsky, 1984), several refinements were performed allowing only the Fe^{3+}, Mg^{2+} and Al^{3+} site occupancies to vary but keeping the total amount of each cation on both the 8*a* and the 16*d* sites consistent with the chemical composition.

For each cation distribution a number of electrons (e^-) per site may be estimated according to

$$n_e(s) = \frac{\sum_i(x_{si} \times n_i)}{m(s)} \tag{1}$$

where x_{si} is the number of *i* ions on the site *s* per unit cell; n_i the number of electrons of cation *i* and $m(s)$ the multiplicity of site *s*. The best agreement factors were always obtained for cation distributions (Table 3) corresponding to 17.0(5) $e^-/8a$ site and 16.1(5) $e^-/16d$ site.

Average cation radii based on the effective ionic radii in the oxide spinels (O'Neill and Navrotsky, 1983) were calculated for each distribution according to

$$\rho_s = \frac{\sum_i(x_{si} \times \rho_{si})}{\sum_i x_{si}} \tag{2}$$

where ρ_{si} is the effective ionic radius of cation *i* with coordination adequate to site *s*. These radii were estimated assuming the O^{2-} radius to be $r_O = 1.38$ Å.

The interatomic distances between a cation and the nearest anion are given for the 8*a* and the 16*d* site, respectively, by (e.g. O'Neill and Navrotsky, 1983)

$$d_{8a} = a\sqrt{3}(u - 0.125) \tag{3}$$
$$d_{16d} = a\sqrt{(3u^2 - 2u + 0.375)} \tag{4}$$

and from these values cation radii (hereafter referred to as structural radii) may be estimated taking

$$r_{8a} = d_{8a} - r_O \text{ and } r_{16d} = d_{16d} - r_O \tag{5}$$

Considering that the uncertainties of the effective ionic radii of O'Neill and Navrotsky (1983) are $\leqslant 0.01$ Å and those of the interatomic distances are $\leqslant 0.001$ Å (cf. standard deviation of *u* and *a* in Table 2), the values of r_{16d} and ρ_{16d} (Table 3) are the same within experimental error but those estimated for the 8*a* site ρ_{8a} are significantly smaller than the corresponding r_{8a}. This is not surprising considering that vacancies are almost exclusively found on the 8*a* sites and estimated d_{8a} values are usually larger when there is a vacancy than when there is a cation on the 8*a* site (Chassagneux *et al.*, 1985; Basso *et al.*, 1991). Considering cation distribution (1) in Table 3 and the

TABLE 2. Crystal data and details of crystal structure refinement

Space Group	$Fd\bar{3}m$, (No. 227)
a	8.2052(4) Å
2θ range	$2°-119°$
ω-2θ scan	$\Delta\omega = 0.80 + 0.35\ \tan\theta$
Approximate crystal dimensions (mm)	$0.09 \times 0.09 \times 0.07$
Data set	$0 \leqslant h \leqslant 19, 0 \leqslant k \leqslant 19, 0 \leqslant l \leqslant 19$
Total data	1166
Unique data	236
Observed data $(Fo \geqslant 4\sigma(Fo))$, n	186
Number of refined parameters, p	11
Final agreement factors	
$R1 = \dfrac{\sum \|F_0\|-\|F_c\|}{\sum \|F_0\|}$	0.0324
$wR2 = \left[\dfrac{\sum\left[w\left(F_0^2-F_c^2\right)^2\right]}{\sum\left[w\left(F_0^2\right)\right]}\right]^{1/2}$	0.0904
$GooF = \left[\dfrac{\sum\left[w\left(F_0^2-F_c^2\right)^2\right]}{(n-p)}\right]^{1/2}$	1.035
Oxygen positional parameter, u	0.2612(2)
Temperature factors	
$(8a)$ U	0.0077(2) Å^2
$(16d)$ U_{11}, U_{12}	0.0066(1) Å^2, $-0.0003(1)$ Å^2
$(32e)$ U_{11}, U_{12}	0.0098(3) Å^2, 0.0002(2) Å^2
Number of e^- per site (eq. (1))	
$n_e(8a)$	17.0(5) e^- / site
$n_e(16d)$	16.1(5) e^- / site

Isotropic temperature factor expressed as $\exp\left\{-8\pi^2 U\left[\frac{\sin(\theta)}{\lambda}\right]^2\right\}$

Anisotropic temperature factors expressed as $\exp\left\{-2\pi^2(a^*)^2\left[(h^2+k^2+l^2)U_{11}+2(hk+hl+kl)U_{12}\right]\right\}$

O'Neill and Navrotsky effective ionic radii, in order to have $r_{8a} \approx \rho_{8a}$ the distance between a vacancy on the $8a$ site and O^{2-} should be 2.056 Å, similar to the value published for synthetic cation defect chromites by Chassagneux et al. (1985).

Both cation distributions in Table 3 fit equally well the single-crystal XRD data. In any case we may conclude that less than 10% of the total Fe is on the octahedral sites and cation vacancies are almost exclusively found on the $8a$ sites.

Mössbauer spectroscopy

Spectra of both Thetford chromite samples taken either at 298 K (Fig. 2) or at 80 K are identical. They were fitted using the model described in Waerenborgh et al., (1994a):

(i) one quadrupole doublet due to ferric iron (estimated hyperfine parameters in Table 4); the estimated isomer shifts, δ, are typical of octahedrally coordinated Fe^{3+} in chromites and gahnites.

(ii) one distribution of quadrupole splittings with average hyperfine parameters typical of Fe^{2+} on the $8a$ site in spinels.

In contrast to the Mössbauer spectra obtained for synthetic $Zn_{1-x}Fe_xAl_2O_4$ spinels where the presence of octahedral Fe^{2+} was detected by XRD (Waerenborgh et al., 1994a), in the case of the Thetford chromite no evidence of a third contribution to the corresponding Mössbauer spectra was observed. The values estimated for the hyperfine parameters are the same for both Thetford samples. These values as well as site assignments are in good agreement with published data for natural aluminous spinels and chromites (Dyar et al., 1989; Wood and Virgo, 1989; Canil et al., 1990; McGuire et al., 1991; Waerenborgh et al., 1994a,b).

The room temperature Mössbauer spectrum of the Serra Alta chromite (Fig. 2) mainly consists of a quadrupole doublet with δ (Table 4) typical of Fe^{3+}

TABLE 3. Cation distributions on $8a$ and $16d$ sites estimated from structure refinement ($\square$ stands for cation vacancies)

Distribution (1)

$8a$ Fe^{2+} 0.08, Fe^{3+} 3.73, Zn^{2+} 1.35, Mg^{2+} 0.84, Mn^{2+} 0.06, Si^{4+} 0.08, $\square$ 1.86

r_{8a} = 0.556 Å ρ_{8a} = 0.52 Å

$16d$ Cr^{3+} 8.45, Fe^{3+} 0.40, Al^{3+} 6.97, Mg^{2+} 0.15, V^{3+} 0.02, Ti^{4+} 0.01

r_{16d} = 0.583 Å ρ_{16d} = 0.58 Å

Distribution (2)

$8a$ Fe^{2+} 0.08, Fe^{3+} 3.67, Zn^{2+} 1.35, Mg^{2+} 0.99, Mn^{2+} 0.06, Si^{4+} 0.08, $\square$ 1.77

r_{8a} = 0.556 Å ρ_{8a} = 0.52 Å

$16d$ Cr^{3+} 8.45, Fe^{3+} 0.46, Al^{3+} 6.97, V^{3+} 0.02, Ti^{4+} 0.01, $\square$ 0.09

r_{16d} = 0.583 Å ρ_{16d} = 0.58 Å

These distributions are obtained allowing (1) Fe^{3+}, Mg^{2+} and Al^{3+} and (2) only Fe^{3+} site occupation factors to vary and keeping the total amount of each cation on both sites consistent with chemical composition. ρ_{8a}, ρ_{16d} stand for the average cation radii and r_{8a}, r_{16d} for the structural radii calculated according to equations (2) and (3–5) respectively.
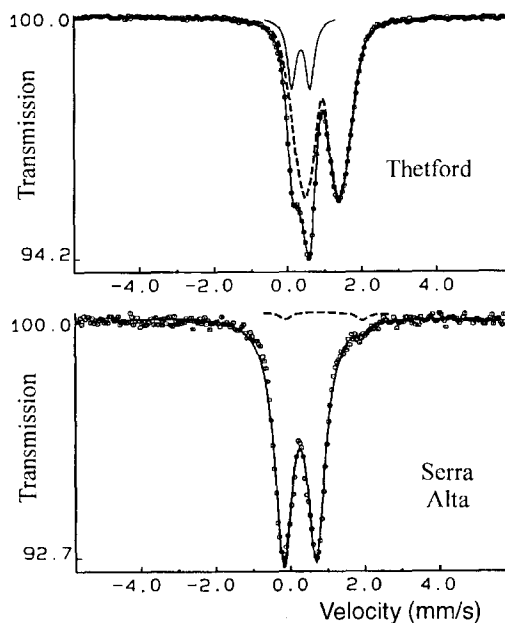

FIG. 2 Room-temperature Mössbauer spectra of the Thetford chromite and the Serra Alta chromite samples. The fitted function is represented on the experimental points. The Fe^{3+} (bold solid lines) and Fe^{2+} (dashed lines) contributions to the spectra are also shown.

in tetrahedral coordination (Gerardin *et al.*, 1985; Schmidbauer, 1987; Wood and Virgo, 1989). The value estimated for the quadrupole splitting, Δ, is significantly larger than those normally found for tetrahedral Fe^{3+} in spinels. It is however not unusual in the case of cation defect chromites (Gerardin *et al.*, 1985; Schmidbauer, 1987). A small contribution (2 $\pm$ 1%) of Fe^{2+} is also present. The estimated value of δ is consistent with tetrahedral coordination but due to the very low relative area of this doublet the accuracy of the estimated δ and Δ does not allow a definitive conclusion.

The spectrum taken at 80 K shows a magnetic splitting with rather broad and in the outer regions somewhat asymmetrical lines which suggests the onset of magnetic ordering at a temperature slightly above 80 K. The difference between the estimated values for δ at 80 K and 298 K is similar to those observed in oxide spinels and namely for the Thetford samples and may be explained by the second order Doppler effect.

Discussion

As far as we know a $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio as high as 0.98 has never been recorded for a natural chromite. We tried therefore to have good experimental evidence that the Mössbauer spectrum of the Serra Alta sample taken at 300 K could only be attributed to a chromite. In fact:

(i) The value of δ estimated for the ferric iron doublet is significantly lower than those observed in

TABLE 4. Hyperfine parameters estimated from Mössbauer spectra taken at 300 K and 80 K

Thetford chromite

	Fe^{3+} on $16d$ site				Fe^{2+} on $8a$ site		
	δ	Δ	Γ	I	$<\delta>$	$<\Delta>$	I
298 K	0.35	0.50	0.28	16%	0.92	1.02	84%
80 K	0.47	0.49	0.36	18%	1.05	2.31	82%

Serra Alta chromite

	Fe^{3+} on $8a$ site				Fe^{2+} on $8a$ site		
	δ	Δ	Γ	I	δ	Δ	I
298 K	0.26	0.88	0.57	98%	0.92	2.06	2%

δ isomer shift given relative to metallic Fe at room temperature (mm/s); Δ quadrupole splitting (mm/s); Γ full width at half maximum (mm/s); $<\delta>$ and $<\Delta>$ average isomer shift and quadrupole splitting of the quadrupole splitting distributions fitted to the Fe^{2+} contribution; I relative areas. Estimated standard deviations are <1% for I and < 0.01 mm/s for the other parameters.

iron oxides/hydroxides with the exception of magnetite where part of Fe^{3+} is found in tetrahedral coordination. Considering the chemical composition of the Serra Alta spinels and the fact that magnetite or maghemite would show long-range magnetic ordering already at room temperature, these oxides may be ruled out.

(ii) Individual grains hand-picked from the material used for the preparation of the Mössbauer absorber were characterized by single-crystal XRD as described above, and although the scarcity of chromite available made it impossible to perform a normal X-ray powder diffraction analysis, a Gandolfi photograph using a few grains was taken (Figueiras and Barriga, 1991). Only chromite with a unit-cell parameter 8.21(1) Å was found and no extra diffraction peaks were observed.

On the other hand, since the Mössbauer spectra of the Thetford chromite obtained with samples without any treatment and after HF treatment were identical, it is reasonable to assume that in the case of the Serra Alta chromite as well, this treatment did not affect the spinel structure and had no influence on the Fe oxidation degree.

Except for Mg and Zn, the differences observed between the columns of Table 1 are much greater than those shown by analyses performed on the same grain. This is taken to mean that each grain has its own average composition. Whether these different average compositions reflect an original variability of a single chromite source or are the result of the contributions of several such sources cannot be

determined with certainty, though we think, based on the published geochemical data set, that the first possibility mentioned is the most probable one.

Likewise, the geochemical environment where these zinc-bearing chromian spinels were formed cannot be determined using the discriminant geochemical plots published in the literature. For most of these plots, the oxidation state of iron (effectively known or deduced from microprobe analyses assuming ideal spinel stoichiometry) is an important parameter and, as far as we know, no natural chromite with all the iron in the Fe^{3+} oxidation state has been reported (the giant database of published chemical data on spinels set up by Roeder (see Roeder, 1994) was used during this study).

The complicated zonation patterns of Zn and Mg lead us to believe that Zn is not an original feature of these chromites, having been introduced during a later alteration episode. Also, the fact that iron is completely oxidized to the Fe^{3+} state, which is unusual, not to say unique, in natural chromites, indicates an alteration feature, not an original one. If both Zn contents and oxidation state of iron are the product of the same alteration process, then it would have attacked Mg in the spinel structure, causing this metal to be partly removed and replaced by Zn and by the vacancies needed to compensate for the simultaneous total oxidation of Fe.

There seem to exist no references in the literature to the physico-chemical conditions under which zinc is incorporated in natural chromite. In the few instances where natural zincian spinels other than

chromite are discussed from this point of view (e.g. Bernier, 1990; Spry and Scott, 1986), their considerations are based on thermodynamical data for spinels (other than chromites) and co-occurring minerals and on the experimental knowledge of the buffering of such parameters as f_{O_2} and f_{S_2} caused by the mineral paragenesis that accompanies spinel. Their conclusions, favouring a relatively low f_{O_2} for the formation of (or the alteration leading to) zincian spinel, can be applied to our case, only if the complete oxidation of iron is not coeval with Zn incorporation. This possibility of two alteration events, one of them introducing zinc and the other one changing the oxidation state of iron would also explain the different zonation patterns observed (while Zn varies erratically, there is virtually no Fe^{2+} present according to Mössbauer spectroscopy and, therefore, no zonation is shown by the oxidation state of iron) and agrees with the common geological observation that chromite is often subjected to late chemical events that oxidize iron, and, most of the times, increase its concentration.

Some geological implications

The mineralogical composition of the quartzites of the South Portuguese Zone, with its overwhelming dominance of quartz and the presence of trace amounts of ultra resistant heavy minerals, leads to the conclusion that the sands where they originated were subject to a very long transportation before final deposition and have its ultimate origin in a sialic metamorphic aluminous continental crust, sometimes with a subordinate and variable contribution from granitic crust.

Yet, the very rare grains of chromite that do occur in some places of the northern half of the South Portuguese Zone (Pomarão, Cela, Melides and Serra Alta) do not seem to be compatible with the just mentioned conclusion. This chromite is chemically 'normal' in all locations except Serra Alta, and is always the sole representative of the paragenesis of the rocks where it may have originated as a primary mineral.

Chromite is fairly resistant to chemical weathering and to mechanical abrasion but it cannot withstand the long transportation indicated by the composition of the rest of the heavy mineral suite. We are thus forced to conclude that chromite has not the same geographical origin as the rest of the minerals. This is equivalent to say that, somewhere along the path followed by sands originating by erosion of a sialic metamorphic terrane, there were one, or several, windows of basic and/or ultrabasic rocks.

In the present geological situation in South Portugal, the only possible sources of chromite are to be found in the Ossa-Morena Zone, but that zone is so close to the present location of the chromitiferous sediments that their maturity and the ultra-resistant character of its mineral contents preclude a direct sediment transportation from this inferred source to the observed final destination, under any normal set of sedimentary/diagenetic conditions. Unusually intense chemical weathering conditions, unreported for Upper Devonian times, able to destroy most of the heavy minerals before deposition, would also decompose chromite in its source rock and so would be incompatible with its presence in the quartzites.

This non-observation of local or regional sources for the quartzitic sediments of the South Portuguese Zone has important implications for our conceptions about the geological evolution of South Portugal.

In the first place, the present higher structural elevation of the Ossa-Morena Zone relative to the South Portuguese Zone did not exist by the time of quartzite deposition. Secondly, the higher textural maturity of the northerly located Serra Alta quartzite when compared to the rest of the South Portuguese Zone quartzites suggests a north-bound transportation of the sands. If this is so, then the ultimate sources of the sediments must lie outside the South Portuguese Zone, in a southern continental block now unknown, and the chromite source should have a continental (as opposed to ophiolitic) nature.

In the discussion above, we implicitly take the absence of chromite from the southern half of the South Portuguese Zone as an artifact caused by its extreme rarity. This is supported by our observation that, at each chromitiferous locality, only one of the collected samples shows chromite. Alternatively, if this absence is taken at face value and if the general contemporaneity of all quartzites is also accepted, as suggested by their great sedimentological and petrographical similitudes and by all the paleontological evidence available, then a mixture of sediments coming from different directions (from the north for chromite and from the south for the sialic metamorphic suite) must be postulated for the chromite-bearing area. This as yet unproved mixture would indicate an intracontinental setting for the deposition of these upper Devonian quartzites since for both streams of sediments a long continental transportation is needed to account for the surviving mineral associations. This is totally inconsistent with current models for the evolution of this segment of the Iberian Variscan Orogen, which see the deformation as caused by a geometrically complex collision between continental blocks, with obduction of parts of the former intervening oceanic crust.

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