Secondary and Backscattered Electron Imaging of Weathered Chromian Spinel

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Summary: Secondary (SE) and backscattered electron (BSE) imaging as well as x-ray microanalysis have demonstrated that the weathering of chromian spinel occurs as a progressive form of alteration. Numerous chemical discriminant analysis methods based on the composition of chromian spinel are used to locate valuable deposits of minerals. These methods will be misleading if the correct interpretation of the weathering of chromian spinel and the subsequent pattern of changes in its mineral chemistry are not properly assessed using scanning electron microscopy. This assessment is vital in understanding the geological processes involved and the economic potential of any indicated deposit. Minerals such as chromian spinel, pyrope garnet, and picroilmenite are considered to be highly resistant to weathering and abrasion and are therefore useful in the search for associated valuable deposits of diamond, nickel, platinum, and gold. Known as indicator minerals, they are usually present in relatively large concentrations compared with the target mineral (e.g., diamond) and form large and often subtle dispersion anomalies adjacent to the deposit. Chromian spinel has long been regarded as a stable indicator mineral; however, detailed SE and BSE imaging indicates that many of the chromian spinels that are routinely examined using scanning electron microscopes (SEM) and microprobes are extensively altered. Secondary electron and BSE imaging of weathered chromian spinel in a normal SEM provides valuable data on the form and chemical style of the alteration. Secondary electron imaging of weathered chromian spinel in the environmental SEM (ESEM) not only enhances the difference in atomic number between unaltered and altered areas but also allows high-resolution imaging of these very fine replacement textures.

Key words: secondary and backscattered electron microscopy, conventional and environmental scanning electron microscopes, chromian spinel, alteration, x-ray microanalysis

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Introduction

Chromian spinel (commonly referred to as chromite) is a black isotropic mineral that often forms perfect octahedra. Its composition, although slightly variable, is of the general form \( (\text{Mg,Fe})_2(\text{Al,Cr})_2\text{O}_4 \). It has no cleavage and fractures as flat surfaces, forming uneven patterns. Chromian spinel crystallises under various pressure and temperature regimes and is commonly found in mafic and ultramafic rocks and their eroded and weathered products. Chromian spinel from altered (serpentinised) ultramafic rocks is often partly or completely replaced by Fe-rich chromite (ferrochromite) around rims and along cracks (Haggerty 1981). This replacement spinel is usually lower in Al and Mg and higher in Fe and Cr compared with the original chromian spinel. This alteration product is normally detected using optical methods and is often confirmed using SE and BSE imaging. During microanalysis, this type of alteration may be easily avoided and only the most pristine parts of the mineral are examined (Pooley 1995). In addition, compositional variations between the pristine core and rim, particularly in broken grains, are also important, and any style of alteration of the original chromian spinel should be avoided.

In highly altered and weathered ultramafic rocks, some chromian spinel grains appear to be fractured and extensively cracked, while others have weathered surfaces often described as “cokey.” Along and adjacent to these areas, the chromian spinel is replaced, forming a chromian spinel that is lower in Mg and Al and higher in Fe and Cr. This replacement proceeds along cracks, microfractures, and possibly dislocations. The correct analysis location is difficult even with the aid of conventional SE and BSE imaging. If these areas of alteration are not avoided during analysis, the compositions derived from these grains will be misleading and their interpretation difficult.

The replacement of the original chromian spinel caused by weathering is not recognisable using optical methods or SE imaging but is discernible by careful examination using a highly efficient BSE detector. Due to the nature of the BSE emission in a normal SEM, these images show excellent atomic number contrast but the fine detail is poorly
resolved. Electron imaging of altered chromian spinels in the ESEM not only enhances the differences in atomic number but also allows high-resolution imaging of these very fine alteration textures. This imaging technique in the ESEM provides unique information on the nature and true extent of chromian spinel alteration and replacement.

Materials and Methods

A number of chromian spinels from different geological environments have been examined using scanning electron microscopy techniques. The chromian spinel grains used here were derived from heavy mineral concentrates of soil and drainage samples taken from Nabberu, Western Australia, and Adminga, South Australia. In addition, a sample of chromitite (spherical aggregate of polygonal chromian spinel grains) was obtained from The Great Serpentinite Belt, near Bingara in New South Wales, Australia.

The chromian spinel grains were coated with 20 to 30 nm of high purity carbon and examined in a JEOL 6400 SEM (JEOL USA, Inc. Peabody, Mass., USA) fitted with an Oxford Instruments Tetra backscattered detector (Oxford Instrument Ltd., Bucks, England). X-ray microanalysis of polished equatorial sections of these grains and polished sections of the chromitite were conducted using a Link-energy-dispersive x-ray spectrometer controlled by an Oxford Instruments ISIS system, to collect and correct the x-ray data for atomic number, absorption, and fluorescence effects. Analyses were conducted at an accelerating voltage of 15 kV, a beam current of 5 nA, and a counting time of 60 s. Uncoated polished sections of the chromitite were examined in an Electroscan E3 ESEM fitted with a modified electron detector (Griffin 1997). Special operating conditions using an accelerating voltage of 30 kV, a working distance of 3.3 mm, and an operating chamber gas pressure of 0.8 Torr were found to achieve the best signal-to-noise ratio at the highest resolution for SE imaging of chromian spinel.

Results

It is noteworthy that none of the alteration patterns described below were visible using light microscopy techniques, nor were they detected using SE imaging in a conventional SEM. It was only when the optimum conditions for BSE imaging were established in a conventional SEM, and the special operating conditions mentioned above were established in the ESEM, that the progressive alteration patterns could be detected.

Progressive Replacement in Chromian Spinel

A common form of alteration in weathered chromian spinel crystals is the massive progressive replacement from the margins of the grain inwards. Often this style of pervasive replacement is complete and none of the original chromian spinel remains. The grain shown in Figure 1a and b has a rough, often termed “cokey,” surface caused by the extensive removal of material from the surface of the grain. Using SE imaging in a conventional SEM, a highly polished equatorial section of this grain shows extreme dissolution in the form of irregular holes, pits, and channel ways throughout the margin of the grain (Fig. 1c). A high-gain BSE image at short working distance indicates extensive changes in the original atomic number of the mineral (Fig. 1d). The chromian spinel is replaced in the margin and near the core of the grain by a chromian spinel that is lower in Mg and Al and higher in Fe and Cr.

These compositional changes in chromian spinel may be expressed in terms of the trivalent ion ratio, Cr/(Cr+Al); Cr# and the divalent ion ratio Fe ²⁺/(Fe ²⁺+ Mg); Fe#. Both ratios are expressed as percentages. The combination of these four ions has been used by numerous investigators to discriminate pristine chromian spinel compositions on the basis of temperature and pressure of formation. Ramsay (1992) examined a number of different chromian spinel compositional domains from different tectonic environments and expressed these domains in the form of such ratios. A number of discrete fields emerged, and the present author has constructed an extended boundary of “chromian spinel significance” (Fig. 2) which generally separates those chromian spinel compositions believed to be in equilibrium with formation of diamond (to the right and generally down from the boundary line) from those believed to be formed at lower pressures and temperatures (to the left and away from the boundary line). Five general types of alteration textures have been observed in weathered chromian spinels using SE and BSE imaging techniques. For convenience, these weathered chromian spinels have been denoted as types A, B, C, D, and E. Examples of the changes in mineral chemistry detected in each of the weathered chromian spinel textural types are shown in Fig. 2.

Figure 2 shows the change in mineral chemistry of a weathered grain of type A chromian spinel. The unaltered composition near the core of the grain (ac) of Cr# = 63.3 and Fe# = 41.3 is markedly different from those areas further away from the core and in the margin of the grain which has a composition of Cr# = 97.2 and Fe# = 54.7 (as) (see Table I; A- ac and A-as). This change in composition is reflected in the change in the atomic number contrast seen in the BSE image (Fig. 1d). If not interpreted correctly, this style of alteration has the potential to change the significance of the original chromian spinel composition from, in this case, not being associated with diamond, to being associated with diamond, particularly if this progressive style of alteration had only progressed to, for example, Cr# = 80 and Fe# = 48, or if the microanalytical area was a mixture of unaltered (ac) and altered (as) chromian spinel regions.

Secondary electron images from a slightly weathered type B chromian spinel grain shown in Figure 3a and b indicate extensive dissolution of material from the entire surface of the grain. The BSE imaging of an equatorial sec-
tion of a larger type B chromian spinel grain indicates two different styles of chemical change (Figs. 2 and 3c). This grain is magmatically zoned with a core composition of Cr\# = 65.9 and Fe\# = 37.3 (bc) and a rim composition of Cr\# = 67.9 and Fe\# = 64.4 (br) (Fig. 2). Two different altered chromian spinel compositions were detected in the margin of this grain: the chromian spinel composition of bs1, where Cr\# = 90.9 and Fe\# = 75.2, represents the alteration of the near rim composition, and the chromian spinel composition of bs2, where Cr\# = 81.0 and Fe\# = 87.5, is believed to represent the alteration product of an original rim composition that was either high in Fe, or possibly altered during different temperature, pressure, or fluid regimes (see Table I; B- bc, B-br, B-bs1 and B- bs2). A BSE image of an area containing a relatively large cavity, caused by a fortuitous pluck of material from the surface of the grain during polishing, reveals a network of fine interconnecting cracks leading away from larger cracks that are visibly associated with altered chromian spinels (Fig. 3d).

Chromian spinel type C is a polygonal grain in a chromite (Fig. 4a and b) and shows a change in mineral chemistry (Fig. 2) from an unaltered composition of Cr\# = 78.0 and Fe\# = 38.2 (c1) to an altered composition of Cr\# = 87.8 and Fe\# = 63.8 (cs). In this case, the alteration has changed the diamond-associated significance of the chromian spinel from relatively high to less attractive. Optimised BSE imaging shows a patchwork of alteration within each grain and thin zones of alteration along margins, fractures, and

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**Fig. 1** (a) Secondary electron (SE) image of the surface of a moderately weathered type A chromian spinel grain taken in a conventional scanning electron microscope. The tips and edges of the crystal are only slightly rounded, indicating that this grain was located very close to its source. Horizontal field width = 200 \(\mu\)m. (b) Facing surface of the grain in more detail. Parts of the original surface of the grain can be seen as flat, smooth faces. Adjacent to these original surfaces are rough and pitted areas caused by the extensive removal of material from the surface of the grain. Horizontal field width = 100 \(\mu\)m. (c) Secondary electron image of a polished equatorial section of the grain shown in Figure 1a. This image shows extensive dissolution of material that has occurred at the edge and margin of the grain. The cavities, pits, and channel ways have acted as conduits for the influx of solutions and the removal of material. Horizontal field width = 100 \(\mu\)m. (d) Backscattered image of the same surface shown in Figure 1 c. The original chromian spinel has reacted to form an altered chromian spinel which is higher in Fe and Cr and lower in Mg and Al. In this image, the increase in contrast is due to the higher atomic number of the altered chromian spinel which has pseudomorphed most of the grain, leaving only a small patchy area in the central portion of the crystal unaltered. Horizontal field width = 100 \(\mu\)m.
cracks (Fig. 4b). Secondary electron imaging in the ESEM not only enhances the contrast of the alteration in these areas but also enables the imaging of very fine detail (Fig. 4c). Figure 4d is an SE image of part of a larger zone of alteration similar to that shown in Figure 4c. At the margins of these zones of alteration, very fine filaments extend out into the unaltered chromian spinel. X-ray microanalysis of the material within the zone of alteration immediately adjacent to these reaction fronts indicates that the altered spinel is higher in Fe, slightly higher in Cr, and depleted in Mg and Al compared with the unaltered host (see Table II; C- c1 and C- cs). Narrow zones of alteration extend throughout the polygonal grains of chromian spinel and link areas of massive alteration (Fig. 4c). These narrow zones have fine diffuse boundaries similar to those shown in Figure 4d and contain small, well oriented pits and holes that are believed to represent areas of dissolution (Fig. 4e). In addition to the zones of alteration, disruptions to the polished surface caused by scratches can be clearly seen.

**Fracture Propagation and Alteration**

The scanning electron micrographs shown in Figure 5 are taken from a slightly weathered type D chromian spinel grain that shows progressive stages of crack and fracture propagation. The SE images (Fig. 5a and b) taken in a conventional SEM show that initially the grain contains a number of relatively large curvilinear cracks that traverse the surface of the crystal. In this case they appear to radiate crudely from an inclusion of serpentine after olivine on the facing surface of the crystal.

**Table I** Compositions of unaltered and altered type A and B chromian spinel grains

<table>
<thead>
<tr>
<th>Description</th>
<th>A-ac</th>
<th>A-as</th>
<th>B-bc</th>
<th>B-bnc</th>
<th>B-br</th>
<th>B-bs1</th>
<th>B-bs2</th>
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**Fracture Propagation and Alteration**

The scanning electron micrographs shown in Figure 5 are taken from a slightly weathered type D chromian spinel grain that shows progressive stages of crack and fracture propagation. The SE images (Fig. 5a and b) taken in a conventional SEM show that initially the grain contains a number of relatively large curvilinear cracks that traverse the surface of the crystal. In this case they appear to radiate crudely from an inclusion of serpentine after olivine on the facing surface of the crystal.

Figure 5c and d shows electron images taken in an ESEM of a polished equatorial section through the crystal at an accelerating voltage of 30 kV, a working distance of approximately 7 mm, and an operating chamber gas pressure of 1.0 Torr. These images show that the curvilinear cracks on the surface of the crystal penetrate through the
crystal in the same curvilinear fashion to produce a relatively coarse anastomosing network of alteration within and immediately adjacent to these cracks. Figure 5d shows that both in and adjacent to these networks the chromian spinel is visibly disrupted by three parallel sets of microfractures. The chromian spinel within and adjacent to these microfracture systems has been altered to be higher in Fe, slightly higher in Cr, and depleted in Mg and Al compared with the unaltered host. The precise nature of the fluid pathways that connect these areas of replacement can be seen clearly in these images. As the alteration proceeds, more of the chromian spinel is infiltrated by a finely divided network of anastomosing microfractures until the entire grain has been replaced by this texture (Fig. 6c and d).

**Formation of Hydrated Fe, Cr oxides**

Figure 6a and b shows SE images of a highly altered type D chromian spinel grain taken in a conventional SEM. The grain exhibits the same form of curvilinear fractures described above despite being thickly coated with a finely porous granular material. Secondary electron and BSE images of a polished equatorial section through this grain show that the entire grain consists of a fine mosaic of microfractures and cracks (Fig. 6c). In another moderately weathered type D chromian spinel grain, BSE imaging (Fig. 6d) shows small “islands” of unaltered chromian spinel (Fig. 2; d1 - Cr\* = 70.5, Fe\* = 75.2, Table II; D-d1). These islands are surrounded by relatively larger masses.

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**Fig. 3** (a) Secondary electron image of the surface of a slightly weathered type B chromian spinel grain taken in a conventional scanning electron microscope (SEM). The tips and edges of the crystal are moderately rounded, indicating that this grain was located at some distance from its source. Horizontal field width = 140 µm. (b) Facing surface of the same grain in more detail. Parts of the original surface of the grain can be seen as small remnants. Adjacent to these original surfaces are numerous areas of dissolution forming an intricate pattern on the surface of the grain. Horizontal field width = 35 µm. (c) Backscattered electron (BSE) image of a polished equatorial section of the slightly weathered type B chromian spinel grain, taken in a conventional SEM. This image shows extensive alteration at the edges of the grain. In one portion of the grain, the alteration has penetrated into the outer margin of the grain via an anastomosing network of microfractures. The core and inner margin of the grain appear unaltered in this image. Horizontal field width = 140 µm. (d) Backscattered electron image of the same surface shown in (c) in more detail. Polishing of the surface of this grain has fortuitously removed a portion of the original surface, exposing a network of microfractures that penetrate deeply from the margin into the outer core of the grain. Immediately adjacent to these fine microfractures the chromian spinel is altered. This network of microfractures is linked to a larger fracture system that traverses the entire section of the grain. Horizontal field width = 70 µm.
of slightly altered chromian spinel (Fig. 2; D, d2 - Cr# = 75.7, Fe# = 78.0, Table II; D-d2) near the core of the grain. The BSE image in Figure 6c shows that at the margins of this grain the extremely fine micro-network of altered chromian spinel has been replaced by a fine, compact, slightly porous hydrated Fe, Cr oxide (Fig. 2; D, dh - Cr# = 93.4, Fe# = 96.0, Table II; D-dh). Backscattered electron images of type E chromian spinel grains show that the formation of the hydrated Fe, Cr oxide is not restricted to the margins of some grains. In other highly weathered chromian grains (Fig. 7), the hydrated Fe, Cr oxide (Fig. 2; E, eh - Cr# = 71.7, Fe# = 90.1, Table II; E-eh) has extended throughout the entire grain leaving only clumps and stringers of the altered chromian spinel (Fig. 2; E, e1 - Cr# = 45.2, Fe# = 80.5, Table II; E-e1).

### Relative Mobility of Elements During Alteration of Chromian Spinel

X-ray microanalysis in a conventional SEM of unaltered and altered chromian spinel types reveals consistent trends in the migration of Fe, Cr, Al, Mg, and Ti in all chromian spinel types studied (see Tables I and II). As alteration proceeds, the Fe content of the altered chromian spinel increases. For example, in type C chromian spinels the Fe2+ ion content increases from 0.386 in the unaltered areas to 0.635 in the altered zones (Table II; C-c1 and C-cs); similarly, the Cr ion content increases during alteration. For example, in type A chromian spinel the Cr ion content increases from 1.249 in the unaltered core of the grain to 1.868 in the margin of the grain (Table I; A-ac and A-as). These increases in Fe and Cr ion contents are offset by the removal of Al, Mg, and Ti during alteration. For example, in type B chromian spinel the Al ion content decreases from 0.678 in the unaltered core to 0.365 in the altered rim of the grain (Table I; B-bc and B-bs2); similarly, in type C chromian spinels the Mg ion content decreases from 0.625 in the unaltered areas to 0.360 in the altered zones (Table II; C-c1 and C-cs).

Titanium is normally partitioned to some degree into the liquid during the growth of a chromian spinel grain and is usually easily detected on a macroscale. Alteration superimposed on magmatic zoning, which is often subtle, can make it difficult to ascertain the relative mobility of Ti during alteration as all the chromian spinels studied had a degree of alteration at the rim of each grain. However, BSE imaging of a type D chromian spinel detected two distinct types of chromian spinel discretely coexisting at a micron level (Fig. 6d). The unaltered chromian spinel has a Ti ion content of 0.021 and the more altered area immediately adjacent has a Ti ion content of 0.011 (Table II; D-d1 and D-d2). In the hydrated Fe, Cr oxides formed at the margin of unaltered chromian spinels; the V, Zn, and Ti contents are relatively much higher compared with the adjacent altered chromian spinels (Table II; D-dh cf. D-d2 and E-eh cf. E-e1), indicating that during the reaction of altered chromian spinel these elements may have been concentrated in the hydrated Fe, Cr oxide product.

### Discussion

The pristine nature of chromian spinel is critical in establishing the original nature of the host rock. Any change in the composition of chromian spinel, particularly Mg, Al, Cr, Fe, Ni, and Zn, will affect interpretation and any subsequent exploration strategy. Valuable mineral bearing rocks such as kimberlite, lamproite, ultramafic lampro-
FIG. 4  (a) Backscattered electron image of a polished surface of a number of slightly weathered polygonal grains of type C chromian spinel in a chromitite taken in a conventional scanning electron microscope (SEM). Some of these grains are altered extensively, others appear altered only along the margin of the grain and in patches. Horizontal field width = 1200 µm. (b) Backscattered electron image of a polygonal type C chromian spinel grain shown in more detail. This grain is slightly altered along margins and cracks and moderately altered in irregular patches. The altered chromian spinel is higher in Fe and Cr and lower in Mg and Al compared with the unaltered chromian spinel. Horizontal field width = 200 µm. (c) Secondary electron (SE) image of a polygonal Type C chromian spinel grain taken in an environmental SEM (ESEM). This is a similar grain to that shown in Figure 4b. The increased contrast of the altered chromian spinel compared with the unaltered chromian spinel allows for the true extent of the alteration to be imaged. Horizontal field width = 120 µm. (d) High-resolution SE image of the interface between altered and unaltered type C chromian spinel taken in an ESEM. The enhanced contrast and resolution of this type of image shows that as the alteration front proceeds, the unaltered chromian spinel (low contrast) is replaced by fine filaments of altered chromian spinel (high contrast). Horizontal field width = 30 µm. (e) High-resolution SE image taken in the ESEM of part of a narrow zone of alteration in the polygonal type C chromian spinel grain shown in Figure 4c. This narrow zone of high contrast has a diffuse boundary with the adjacent unaltered chromian spinel. Oriented pits and holes in these narrow zones of alteration indicate extensive dissolution of material. Horizontal field width = 20 µm. (f) Secondary electron image of part of a polygonal Type C chromian spinel grain taken in an ESEM. Geometric patterns of high contrast are believed to be altered chromian spinel pseudomorphs possibly replacing primary crystal growth and overgrowth textures. Areas of high contrast along the margin of the grain show the progressive nature of the alteration of chromian spinel proceeding inwards from the margin of the grain. Extremely narrow linear features of high contrast are scratches induced by polishing during the preparation of the sample. Horizontal field width = 50 µm.
 PHYRE, and komatiite intrusions are geologically complex, often highly altered, and are located in a variety of geological terrains. Other factors such as the past and present erosional climate and pH of the ground water will also affect the rate and degree of alteration in chromian spinel (Haggerty 1981). Secondary electron and BSE imaging of chromian spinel in a conventional SEM is important in establishing the internal microstructure of altered grains; SE imaging in the ESEM reveals the style and the true extent of the alteration. The improved resolution and extremely high contrast achieved in imaging uncoated polished sections of altered chromian spinel grains in the ESEM compared with images achieved from coated specimens in a conventional SEM is important in establishing the true extent of alteration in chromian spinel.

Thiel et al. (1997) have proposed a model for the gas amplification effect which is used for signal generation in the ESEM and compared its predictions with experimental data. In particular, their model indicates that the background components of the total detected signal, due to BSE from the specimen and to primary beam electrons, increase with gas pressure, and that part of the signal, resulting from the specimen’s SE emission, is not inherently dependent on gas pressure. This work suggests that, provided sufficient gas is present to provide charge neutralisation at the surface of chromian spinel as the gas pressure is reduced, the proportion of the total signal due to secondary emission will increase. In the case of altered chromian spinel, the variation in composition between unaltered and altered chromian spinel, demonstrated by conven-

![Fig. 5](image_url)

Fig. 5  (a) Secondary electron (SE) image of the surface of a slightly weathered type B chromian spinel grain taken in a conventional scanning electron microscope (SEM). The tips of the crystal are slightly rounded and the edges are almost intact, indicating that this grain was located in the weathering profile of the source material. The facing surface of the crystal is traversed by a pattern of curvilinear cracks. Horizontal field width = 170 µm. (b) Secondary electron image showing more detail of the facing surface of the crystal in Figure 5a. The inclusion in the centre of the face of the crystal is a pseudomorph of serpentine after olivine. The alteration of the olivine is believed to be the result of the weathering process and is probably related to the alteration of the host chromian spinel. Horizontal field width = 55 µm. (c) Electron image of a polished equatorial section of the chromian spinel grain shown in Figure 5a taken in the environmental SEM using a nonpassivated solid state electron detector. This image shows that the entire surface of this section of the grain is traversed by a network of curvilinear cracks. These cracks are similar to those shown on the crystal surfaces in Figure 5a and are believed to be part of the same network of curvilinear cracks. Horizontal field width = 100 µm. (d) Part of the crack network in Figure 5c in more detail. This image shows that these cracks are associated with three sets of microfractures that appear within and immediately adjacent to the cracks. This image also shows that the original chromian spinel has been altered in zones (slightly higher contrast) along and adjacent to these microfractures. Horizontal field width = 40 µm.
tional SEM backscattered images and x-ray maps, correlates with SE image contrast from an uncoated specimen in the ESEM. However, imaging in the ESEM with this type of SE signal results in a higher resolution image as it is closer to a pure SE (SE1) image.

More recently, Watt et al. (2000) have presented SE images of minerals such as zircon, quartz, biotite, and cordierite taken in an ESEM and referred to these images as charge contrast images. They explain that due to the limited suppression of SE1 electrons at lower gas pressures by the positive ion flood, the images are dominated by SE1 emission and defect-rich regions will appear brighter as they generate more SE1 electrons. Charge contrast images of zircon, quartz, biotite, and cordierite show compositional and microstructural contrast information similar to those observed when imaging chromian spinel in the ESEM. In particular, relict fluid pathways in chromian spinel connecting areas of more massive alteration (Fig. 4c and e) are clearly visible using this type of imaging in the ESEM. This, coupled with the ability to image fine replacement reaction fronts at relatively high resolution (Fig. 4d), provides valuable data on fluid access in chromian spinel and the true nature of the alteration process.

In the case of chromian spinel, the excellent SE contrast achieved between unaltered and altered areas in chromian spinel in the ESEM is more likely to be due to the increased

Fig. 6 (a) Secondary electron (SE) image of the surface of a highly weathered type D chromian spinel grain taken in a conventional scanning electron microscope. The grain is coated with a porous finely granular material consisting of an hydrated Fe, Cr oxide. This grain has not travelled far from the site where the coating was formed. Horizontal field width = 250 µm. (b) Facing surface of the grain in Figure 6a in more detail. Parts of the original cracks similar to those shown in Figure 5a can be seen on the grain slightly below the surface of the outer coating. Horizontal field width = 70 µm. (c) Backscattered electron (BSE) image of a polished surface near the margin of the grain shown in Figure 6a. The original chromian spinel is completely altered throughout the entire grain. The altered chromian spinel (high contrast) consists of an extremely finely divided anastomosing network of microfractures at the margin of the grain; this texture is typical of type D chromian spinels. At the extreme margin of the grain, the altered chromian spinel has been replaced by a fine porous material consisting of an hydrated Fe, Cr oxide that has retained the fine anastomosing texture of the adjacent altered chromian spinel. Horizontal field width = 50 µm. (d) Optimised BSE image of a polished surface near the core of a moderately weathered type D chromian spinel grain. This image shows relict islands of unaltered chromian spinel (low contrast) surrounded by altered chromian spinel (high contrast) in a relatively coarse anastomosing network of microfractures. Horizontal field width = 50 µm.
stopping power associated with the higher average atomic number of the altered areas. In addition, differences in SE yield of conductors, semiconductors, and insulators have been documented by many workers (e.g. Bruining 1954; Kanaya and Ono 1984), and possibly the excellent SE contrast achieved in the ESEM may be partly due to the relative poorer electron conduction and therefore possible higher SE yield associated with the unaltered areas. In Type C, chromian spinels (Fig. 4c and d) have an unaltered composition of Cr$^\# = 78.0$ and Fe$^\# = 38.2$ (darker areas) and an altered composition of Cr$^\# = 87.8$ and Fe$^\# = 63.8$ (brighter areas)—see Table II: C-c1 and C-cs. This difference in composition may possibly also indicate a difference in band-gap energy and microstructure between the two areas, resulting in a relative poorer electron conduction associated with the unaltered areas which in the ESEM, using this style of imaging, provides an enhanced SE contrast which is very sensitive to the alteration process.

Damaged areas such as scratches induced by polishing also show an increase in contrast (Fig. 4f). This type of contrast is most likely due to electron side-scattering from the scratch channel. A further contribution to this increased contrast is probably due to the different electron conduction characteristics caused by the surface and near surface disruption of the crystal structure along and immediately adjacent to the scratches.

**Conclusion**

Secondary electron imaging of chromian spinel in the ESEM reveals alteration, growth structures, areas of crystallographic dislocation, and chemical change on a micron scale. This imaging not only enhances the differences in atomic number but also allows high-resolution imaging of very fine replacement textures. The high-contrast images of altered chromian spinel obtained in the ESEM are also believed to reflect differences in band structure and therefore differences in SE emission. This technique provides unique data on the nature and true extent of alteration in chromian spinel. For example, in the geological exploration for diamonds, exploration strategies require a rapid turnaround in the determination of chromian spinel composition using electron microprobes. On these instruments, the location of the analysis point is often determined using light microscopy or conventional SE imaging. Furthermore, these instruments are commonly operated in an automatic (unattended) mode, relying on the certainty of electronic positioners to relocate the desired analysis point accurately. The subtle replacement textures and subsequent changes in mineral chemistry in chromian spinel described above will not be avoided using this traditional method of electron microanalysis.

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**References**


