SPINEL CHEMISTRY AND PETROGENETIC PROCESSES IN THE TAPIRA ALKALINE-CARBONATITE COMPLEX, MINAS GERAIS, BRAZIL

JOSÉ AFFONSO BROD1,2, JOSÉ CARLOS GASPAR1,2, HENRIQUE SENNA DINIZ-PINTO1,2 & TEREZA CRISTINA JUNQUEIRA-BROD1,2

Abstract The Tapira complex, SE Brazil, is part of the Late-Cretaceous Alto Paranaiba Igneous Province (APIP), and consists of a Silicate Plutonic-rock Series (SPS, comprising wehrlites, bebedourites and syenites) and subordinate carbonatites. Two major units of coarse-grained ultramafic rocks (B1 and B2) and five groups of carbonatites (C1 to C5) occur in the complex. The plutonic rocks are crosscut by ultramafic fine-grained dykes (phlogopite picrites and bebedouritic dykes). Spinell composition is intimately related to magma evolution, reflecting both crystal fractionation and liquid immiscibility processes. Spinell-group minerals evolve from chromite through ulvospinel to magnetite with magma fractionation and high-Cr spinell is a reliable indicator of the most primitive rocks in the complex (phlogopite picrites). Spinell chemical variations agree well with other (field, petrographic and geochemical) evidence, which indicate magmatic evolution from B1 to B2 in the SPS and from C1 to C5 in the carbonatites. Spinels from some Tapira wehrlites cannot be attributed to fractionation from phlogopite picrites or bebedourtic magmas. These wehrlites are more likely to have been produced by crystal fractionation from unevolved immiscible carbonate-rich liquids, rather than from their silicate-rich counterparts.

Keywords: APIP, carbonatite, bebedourite, wehrlite, chromite, magnetite,

INTRODUCTION The Tapira complex is located in the western portion of the State of Minas Gerais, SE Brazil, immediately to the north of Tapira village and approximately 30 km south-southeast of the city of Araxá. It is the southernmost of a series of Late-Cretaceous, carbonatite-bearing alkaline plutonic complexes which, together with kamafugites and kimberlites, form the Late-Cretaceous Alto Paranaiba Igneous Province (APIP, Gibson et al. 1995). The complex intrudes phyllites, schists and quartzites of the Neoproterozoic Brasília mobile belt, adjacent to the São Francisco craton.

Primary magmatic opaque minerals present in Tapira rocks comprise mainly spinel-group minerals, and rare ilmenite. Magnetite is by far the most abundant species, occurring in both carbonatites and silicate rocks. Ulvospinel is only present in the silicate rocks. Chromite is restricted to phlogopite picrites and, occasionally, to wehrlites.

In this paper we aim to describe and interpret the composition and evolution of spinel-group minerals from several Tapira rock-types in the light of the petrogenetic processes such as crystal fractionation and liquid immiscibility.

GEOLOGY AND PETROGRAPHY The Tapira complex is roughly elliptical (Fig. 1), 35 km² in area, formed by the amalgamation of several intrusions of dominant plutonic silicate rocks, with less voluminous carbonatites and ultramafic dykes.

The silicate plutonic-rock series (SPS) consists mainly of bebedourite, with subordinate wehrlite and syenite, and rare dunite and melilitolite. At least two separate units (B1 and B2) of coarse-grained ultramafic rocks are recognised within the SPS. The B1 unit occupies most of the central portion of the complex and is partly surrounded, at the northern margin, by B2. Coarse- to medium-grained syenites occur as an intrusive body in the northern portion of the complex, and as smaller plugs elsewhere.

Five episodes of carbonatite intrusion (C1 to C5) were identified. The earliest and largest carbonatite (C1) occurs at the centre of the complex, intruding B1. Recent drillings near this area exposed significant occurrences of phoscoritic rocks, which are probably associated with the C1 carbonatites. C2 carbonatites form an intrusive body geographically associated with syenites, in the northern part of the complex, but occur also as scattered dykes.

Figura 1 - Geological sketch of the Tapira complex, based on drill core information. No drill cores were available for the white areas in the southwestern and eastern portions of the complex (After Brod 1999)

1 - Universidade de Brasilia, Instituto de Geociências, 70.910-900 - Brasilia, DF - Brazil
2 - CNPq - Conselho Nacional de Desenvolvimento Científico e Tecnológico
3 - Companhia Vale do Rio Doce
and as minor diatreme-like breccias elsewhere. C3 and C4 are small intrusions, respectively located near the northern and southern margins of the complex. C5 comprises widespread late-stage dykes and veinslets. A general progression in composition is observed from C1 to C4, starting with dolomite-bearing slivers (C1 and C2) and evolving towards pure sövite (C3 and C4). Dolomite-rich carbonatites (beforulite) are recurrent in the late-stage C5 dykes.

All plutonic rock-types are crosscut by fine-grained ultramafic dykes. These are carbonate-rich and may contain carbonate ocelli, indicating that immiscibility between carbonate and silicate liquids occurred early in the evolution of the complex (Brook 1999). Two varieties are recognised: the most primitive dyke-rocks have been named phlogopite picrites (Gibson et al. 1995), and consist of olivine phenocrysts in a groundmass of phlogopite, carbonate, perovskite, oxides and apatite. Ultramafic dykes of the second variety typically lack olivine and Cr-rich spinel, and are compositionally similar to the coarse-grained bebedourites of the SPS, representing more evolved (although still ultramafic) liquids. Therefore, these are termed here bebedouritic dykes. The primitive Tapira magmas are ultrapotassic and have a strong geochemical affinity with APIP kamafugites (Brook et al. 2000).

**Wehrsites and other olivine-bearing cumulates**

A small percentage of the samples collected from the SPS contain olivine. In the B1 unit, some of these are wehrsites, but variations towards olivine-bearing apatite- and/or perovskite-rich cumulates are also common. Although rare dunites can be found at the present exposure level, samples were too strongly serpentinised to allow petrographic or chemical studies. Some of the Tapira wehrsites could represent a less evolved version of the largely dominant bebedourites, while other wehritic cumulates, especially those which grade into apatite- and magnetite-rich cumulates appear to be more closely related to the phoscorite series (Brook et al. 2004) and, therefore, could be related to carbonatitic activity in the complex.

Most samples lack preferred mineral orientation but igneous layering is evident in some cases, particularly in apatite- and perovskite-rich rocks. The textural relationships between the essential minerals suggest crystallisation in the sequence (Brook 1999):

- olivine (± chromite) → apatite → perovskite → clinoxyroxene → phlogopite + magnetite

Two varieties of opaque minerals are present. In the more olivine-rich samples, they occur as small interstitial chromite crystals, usually associated with perovskite. In more evolved cumulates Ti-rich magnetite is dominant. Chromite is the only abundant phase to occur as microinclusions in olivine, which testifies to its early-stage crystallisation. Perovskite and chromite or magnetite may locally form aggregates of small equant grains coating olivine crystals (Fig. 2). Magnetite is Ti-rich, occasionally developing exsolution lamellae of ilmenite.

Olivine-bearing cumulates were not found in the studied drill cores within the B2 unit. Nevertheless, a few wehrsite dykes intrude the B1 bebedourites and were assigned to the B2 unit, on the basis of mineralogical and petrographic similarities with other B2 rock-types. These wehrsites are medium to fine grained, composed essentially of olivine, clinoxyroxene, melanite, phlogopite, apatite and opaque minerals. A fundamental difference between B1 and B2 wehrsites is that the latter contain only minor amounts of perovskite, but have abundant primary Ti-garnet (melanite to schorlomite). Olivine contains abundant inclinations of euhedral apatite, and the overall textural relationships suggest the following crystallisation order between essential phases in B2 wehrites:

- apatite → olivine → diopside → garnet + phlogopite + magnetite

The presence of primary Ti-garnet, together with the paucity of perovskite indicate that the magma from which B2 wehrites derived had a higher silica content than the one associated with the B1 wehrites.

**B1 Bebedourites**

Bebedourite is a rock name proposed by Tröger (1928, quoted in Tröger 1935) to designate an alkaline clinopyroxenite rich in diopside, biotite, perovskite and opaque minerals, with accessory apatite, K-feldspar and olivine. The type locality for bebedourite is the Salitre alkaline complex, in the APIP. Bebedourite is a very conspicuous rock-type in all large plutonic carbonatitic complexes of the province (Brook et al. 2004) and also occurs as xenoliths in the kamafugitic Mata da Corda pyroclastic deposits, thus reinforcing the kamafugitic-carbonatite association in the Alto Paranába Igneous Province (Brook et al. 2000).

In the Tapira complex, B1 bebedourites comprise essential diopside, perovskite, apatite, phlogopite and magnetite. Olivine and chromium-rich spinel are typically absent. Melanite, carbonate and rare zirconolite may occur in accessory amounts. In particular, the occasional presence of zirconolite and the abundant perovskite, are strong indicators of silica-undersaturation in the magma that produced these rocks. The opaque minerals are a relatively late-crystallising phase in B1 bebedourites, forming at the same time as, or after, phlogopite, in which case they are typically interstitial and anhedral.

Texturally, B1 bebedourites are medium to coarse-grained, locally pegmatitic. Modal layering is often present and faces variations due to major changes in modal composition are not uncommon. Marked changes in the crystallisation order appear with magma evolution in B1 bebedourites. In the least evolved variants it follows the sequence (Brook 1999):

- diopside → perovskite → olivine → phlogopite + magnetite

In the more evolved rocks this changes to:

- diopside → perovskite → olivine → magnetite + phlogopite.
B2 Bbedourites. The B2 bebedourites are usually finer-grained and have higher clinopyroxene content than those of B1. Densely packed accumulations of diopside crystals with intercumulus phlogopite are common. Apatite, perovskite, melanite and titanite are usually present in subordinate amounts. The crystallisation sequence varies with magmatic evolution. At the very early stages the order appears to be:

apatite + perovskite → diopside → phlogopite + magnetite → garnet → titanite.

This is later replaced by:

diopside → (± perovskite) → apatite + phlogopite + magnetite + garnet + titanite → (± K-feldspar)

which is the dominant sequence in B2 bebedourites. Similarly to B1, these bebedourites may show strong mineral orientation, although this is a less common feature in the B2 unit.

B2 rocks formed under higher SiO₂ activity than B1. This is supported by the following evidence: a) primary garnet in wehrlite dykes; b) primary titanite and garnet in the bebedourites; c) primary (intercumulus) K-feldspar in perovskite-free, evolved bebedourites; d) low modal content of perovskite throughout the B2 unit; and e) disequilibrium features of the existing perovskite, which is invariably replaced by Ti-rich silicate minerals or oxides (Brod 1999).

Increase in silica content of a differentiating magma is normally expected, and would be consistent with B2 rocks being more evolved than B1. However, the occurrence of Ti-garnet, rather than perovskite, in the - presumably - less differentiated wehrlites suggests that this variation was not smooth, but probably disturbed by oscillations in the silica activity of the system. These composition oscillations could have been controlled by one or more of the following processes: a) preferential removal of silicate (olivine, clinopyroxene) or non-silicate (perovskite, oxides, apatite) phases; b) assimilation of the quartzitic country rock, as suggested by the excess of radiogenic Sr and Nd in some ultramafic dykes (Brod et al. 1999) and of rounded quartz xenocrysts in carbonatite dykes (Brod 1999), causing uneven silica distribution in the liquid; or c) involvement of Tapira magmas in one or more episodes of carbonate-silicate liquid immiscibility.

Carbonatites. The Tapira carbonatites were grouped into five different units (C1 to C5), according to their location in the complex (Fig. 1) and to their mineralogical and petrographic properties. Temporal relations between these bodies are difficult to estimate from drill core data alone. Therefore, the sequential numbers were attributed to the units on the basis of limited indirect evidence, such as the spatial association with particular units of the SPS, and the chemistry of key mineral phases.

The C1 unit is the largest carbonatite area in Tapira and consists essentially of sôvites and dolomite-sôvites intruding the ultramafic rocks of the B1 unit, near the centre of the complex. C1 carbonatites are granular, medium-grained, and vary from homogeneous to locally banded. The essential minerals are calcite, phlogopite, magnetite and apatite, whereas dolomite, sulphides, barite and pyrochlore occur in subordinate amounts. Two varieties of magnetite are present. One consists of medium-grained crystals scattered in the carbonatite, invariably showing ilmenite exsolution lamellae. The other variety comprises very fine-grained magnetite, interstitial to carbonate grains, displaying no visible signs of exsolution.

The C2 unit occurs as: a) an independent intrusion, geographically associated with syenites in the centre-north region of the complex (Fig. 1); and b) as dykes and diatreme-facies breccias elsewhere in the complex. These rocks are typically associated with syenites. C2 rocks are usually finer-grained than C1 and consist essentially of carbonate, with accessory magnetite and very small (in most cases negligible) amounts of phlogopite, amphibole, zirconolite, barite and pyrochlore. Opaque minerals comprise small interstitial grains of subhedral magnetite, with subordinate amounts of relatively coarser-grained sulphides, mostly pyrite.

Globules composed of fine-grained feldspathic aggregates are common in C2 fine-grained dykes, suggesting that this carbonatite unit is related to syenites by liquid immiscibility.

C3 unit occurs in the northern extremity of the complex and is geographically associated with B2 bebedourites, appearing to intrude right at the contact between B2 and a small area of B1 bebedourites (Fig. 1). This unit consists of isotropic, granular, medium- to coarse-grained calcite-carbonatites, with subordinate rounded crystals of apatite. Magnetite is common, and xenocrysts of diopside and phlogopite are conspicuous (Brod 1999). Perovskite is an extremely rare accessory in C3.

The C4 unit is petrographically similar to C3, except for the absence of diopside xenocrysts. It crops out in an isolated area, where the contact with the country rock is not exposed.

The C5 unit encompasses a number of late-stage thin dykes and veins scattered throughout the Tapira complex, and is considered to represent the youngest carbonatite activity in the complex. These rocks are particularly common in the area marked C5 in figure 1, probably representing a larger dyke or system of dykes near the northwestern border of the complex. C5 carbonatites are usually fine-grained and equigranular, composed of dolomite or mixtures of dolomite and calcite. Magnetite and barite are common. Apatite and xenocrystic phlogopite are very rare.

Ultramafic dykes. The plutonic rocks of the Tapira complex are crosscut by a large number of ultramafic dykes, usually a few centimetres thick, but exceptionally reaching a few metres. These rocks can be subdivided, on the basis of their mineralogical and chemical characteristics (Brod 1999) into phlogopite picrites and bebedouritic dykes.

PHLOGOPITE PICRITES. Phlogopite picrites consist of subhedral to euhedral olivine (less frequently phlogopite, apatite, clinopyroxene or perovskite) phenocrysts set in a fine-grained groundmass composed of phlogopite, carbonate, apatite, perovskite and opaque minerals. They show accumulation of olivine phenocrysts towards the centre of the dykes by flow-differentiation.

Opaque minerals in the phlogopite picrites comprise chromite and Ti-rich magnetite, usually as small scattered grains in the groundmass. Another variety comprises slightly larger, equant crystals which, together with perovskite, form a coating on olivine phenocrysts, a texture identical to that observed in B1 wehrlites (e.g. Fig. 2). These are interpreted as the nucleation of primary perovskite and spinel against olivine phenocrysts, and may have been transferred to the cumulates with the olivine. Many spinel-group minerals in the phlogopite picrites show complex zoning and form skeletal crystals (Fig. 3).

Carbonate "pockets" of irregular or globular shape suggest that immiscibility of carbonate-rich liquid from the phlogopite picrite magma may have occurred as early as the olivine crystallisation stage. Some of the features shown in figure 3, such as the coexistence of titanite and perovskite (although they are not in mutual contact) indicate sudden and dramatic changes in silica.
Figure 3 - Back-scattered electron (BSE) images of spinel-group minerals in phlogopite picrites. **Upper left:** Zoned spinel crystal, composed of a Cr-rich core (Cr-Mag) and a Cr-poor, Ti-rich (Ti-Mag) rim. Note the titaniaite (Sph) inclusions, prevented from reacting with the silica-saturated liquid by the Ti-magnetite rim, and the perovskite (Pv) inclusions, which probably nucleated against the Cr-rich core. **Upper right:** Cr-rich (Cr-Mag) core, overgrown by a titanite (Sph) rim which is, in turn, isolated from the groundmass by an external rim of Cr-poor magnetite (Mg). Note the perovskite (Pv) crystals nucleated against the magnetite. **Lower left:** Skeletal zoned spinel crystal composed of a Cr-rich core (Cr-Mag), followed by a Ti-rich zone (Ti-Mag) and an outer rim of Cr- and Ti-poor magnetite (Mg). Inclusions comprise the very fine-grained phlogopite picroitte groundmass material (Gm) and some crystals of groundmass calcite (Cc) and perovskite (Pv). **Lower right:** Zoned skeletal crystal composed of a Cr-Ti-rich core (Cr-Ti-Mag), followed by Cr-poor, Ti-rich zone (Ti-Mag) and a Cr-poor and Ti-poor (Mag) outer rim. Abundant inclusions of groundmass (Gm) relics and fine-grained perovskite (Pv) and titaniaite (Sph).

activity of the liquid, which is consistent with liquid immiscibility processes.

**BEBEDOURITIC DYKES** These rocks typically contain phenocrysts of one or more of pyroxene, apatite, garnet and phlogopite, set in a groundmass of the same minerals plus magnetite and carbonatite. With the magmatic evolution of these dykes, the carbonate content progressively increases in the groundmass, often leading to the formation of carbonate globules or ocelli, which are interpreted as evidence of liquid immiscibility, in the same way as with the phlogopite picrorites. In some cases, groundmass carbonate enrichment is extreme, and the rock virtually grades into a silico-carbonatite.

**SPINEL CHEMISTRY** Electron microprobe analyses of spinels from Tapira wehrlites, bebedourites, carbonatites, phlogopite picrorites and bebedouritic dykes were carried out at the Universities of Brasilia and Cambridge, using CAMECA SX-50 microprobes equipped with three WD spectrometers and one ED system, operating at 20 nA and 20 kV. Table 1 shows examples of representative spinel-group mineral analysis, for the various studied rock-types.

Spinel-group minerals occurring in the coarse grained plutonic rocks (SPS and carbonatites) are compositionally distinct from

Figure 4 - Fe\(^2+\)/Fe\(^3+\) + Mg) plotted against Fe\(^2+\)/(Fe\(^3+\) + Al + Cr) for spinels from Tapira wehrlites, bebedourites and ultramafic dykes.
Table 1 - Representative spinel composition from various Tapira rock-types (1 – phlogopite picrite, 2 – bebedouritic dyke, 3 – wehrlite, 4 – B1 bebedourite, 5 – B2 bebedourite, 6 – C2 carbonatite, 7 – C3 carbonatite, 8 – C4 carbonatite).

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Cations on the basis of 32 O

Si 0.0436 0.0670 0.0105 0.0099 0.0356 0.3010 0.0349 0.0396
Ti 1.6690 2.6354 1.9828 1.7445 0.4283 2.3183 1.2375 0.6993
Al 1.4282 0.3985 0.3232 0.0072 0.0122 0.1745 0.0374 0.0216
Cr 7.5555 0.0093 0.6768 0.0041 0.0206 0.0046 0.0201 0.0241
Fe³⁺ 5.4315 7.9662 8.2361 9.4293 8.0755 10.1176 8.6460 7.2749
Mn 0.0659 0.1811 0.3229 0.1521 0.2142 0.0141 0.3479 0.2427
Mg 4.2213 2.5032 1.4267 0.2270 0.1260 0.1818 0.2699 1.1952
Ca 0.0000 0.0518 0.0076 0.0059 0.0482 0.2159 0.0068 0.0261

Those in the fine-grained dyke rocks (phlogopite picrites and bebedouritic dykes). The following discussion attempts to cover spinel composition from the widest possible range of Tapira rocks. However, the discussion on carbonatite spinels will be focused only on C2, C3 and C4 carbonatites. The reason for this is that C1 spinels typically show ilmenite exsolution, making it difficult to assess the composition of the primary spinel. On the other hand, the very fine grain-size in spinel-group minerals in C5 carbonatites, and the fact that these rocks have been actively involved in various late-stage events in the complex, do not allow to securely establish the primary character, or otherwise, of C5 spinels.

Figure 4 shows the composition of spinel-group minerals from Tapira silicate rocks. Spinels from phlogopite picrites and bebedouritic dykes form a continuous trend, starting from Cr-(and Al-) rich and evolving through relative increase in Fe³⁺, which reflects progressive enrichment in the magnetite end-member. Most analyses appear to follow a trend of steeper increase in Fe³⁺/(Fe³⁺+Al+Cr) than in Fe²⁺/(Fe²⁺+Mg), until the first ratio reaches values close to 1. This reflects the rapid decrease in Cr and Al, and increase of Fe³⁺, within a comparatively short range (0.5 to 0.7) of Fe²⁺/(Fe²⁺+Mg) (Figs. 5-7). For Fe³⁺/(Fe²⁺+Mg) higher than 0.7, the spinels in phlogopite picrites and bebedouritic dykes contain very little of both Cr and Al, and their evolution becomes insensitive to Fe³⁺/(Fe³⁺+Al+Cr). However, a few samples seem to follow a trend of steady increase in both ratios in figure 4, progressing directly to the magnetite component. This latter trend seems to coincide with the alignment of some analyses from wehrlites.

Figures 5 to 7 are plots of Fe³⁺/(Fe³⁺+Mg) against the trivalent cations. Spinels from phlogopite picrites and wehrlites may show appreciable Cr content (up to 9.3 atoms per formula unit), while spinels from Tapira bebedourites, carbonatites, bebedouritic dykes and some relatively evolved phlogopite picrites are virtually Cr-free. Spinels from phlogopite picrites show a steep trend of decreasing Cr contents up to a Fe³⁺/(Fe³⁺+Mg) value of ca. 0.7, evolving as Cr-free spinels from this point on (Fig. 5). Spinels from wehrlites also show a trend of decreasing Cr, although with a slightly wider scatter, and at significantly higher Fe³⁺/(Fe³⁺+Mg) values (0.8 to 0.97).

The behaviour of Al (Fig. 6) is similar to that of Cr, although Al decreasing is less steep and many magnetites from phlogopite picrites, bebedouritic dykes, wehrlites, and carbonatites still have some Al even at the highest Fe³⁺/(Fe³⁺+Mg). Spinels from bebedourites (B1 and B2), on the other hand, are virtually Al-free.

Tapira spinels show a general trend of Fe³⁺ increase with Fe²⁺/(Fe²⁺+Mg). However, from Fe³⁺/(Fe²⁺+Mg) = 0.7, the trend is shifted to slightly higher Fe²⁺/(Fe²⁺+Mg) values, and the scatter increases considerably, although this is not necessarily the case within a single rock-type (Fig. 7).

Figure 8 shows that, in terms of trivalent elements, spinels from Tapira silicate rocks may be divided in at least three separate trends. In phlogopite picrites, spinels evolve initially by simultaneous Cr and Al decrease. This trend reflects an evolution
from Cr-rich to Cr-poor spinel at relatively constant Al. Only after most of the Cr is consumed in the crystallising liquid, the Al content in these spinels starts to decrease again, now at constantly low Cr levels. A second trend may be defined by spinels from bebedourites and bebedouritic dykes, which evolve by Al decrease and Fe\(^{3+}\) increase, and are virtually Cr-free throughout. They thus correspond roughly to the second part of the phlogopite picrite trend (at even lower Cr values) and are plotted together with the phlogopite picrites in the left diagram of figure 8. A third group of analyses comprises the wehrlites, whose spinels evolve through Cr decrease and Fe\(^{3+}\) increase at typically low Al content. The most striking feature of this diagram is that spinels from the phlogopite picrites and bebedouritic dykes may fit into a single evolving trend of decreasing Cr (at first), and then Al, coupled with increasing Fe\(^{3+}\). The composition of wehrlite spinels, on the other hand, is difficult to reconcile with this trend, since they reach the magnetite end-member from the opposite side of the diagram (i.e. Cr decrease and Fe\(^{3+}\) increase at low Al content). Spinels from bebedourite and carbonatite are not plotted, as they cluster near the Fe\(^{3+}\) apex and cannot be distinguished on the adopted scale.

Figure 9 shows the evolution of Tapira spinels in terms of Ti, Fe\(^{2+}\) and Mg for Tapira silicate rocks. Noteworthy from the plots is the Mg decrease and Ti increase at constant Fe\(^{2+}\), observed near the beginning of the trend of phlogopite picrite spinels, and the good agreement between the trends of phlogopite picrites and bebedouritic dykes, although in a limited data range. Spinels from the wehrlites follow an independent trend of continuously decreasing Ti and Mg, and increasing Fe\(^{3+}\). B1 and B2 vary in the same direction as wehrlite spinels, but at lower Mg content. Also note the less evolved character of bebedourites B1 relatively to B2, C2, C3 and C4 show progressively lower Ti, in this sequence, but C4 is shifted from this trend toward slightly higher Mg contents.

Figure 10 relates Ti, Fe\(^{2+}\) and Cr for spinels of various Tapira rock-types. Here, phlogopite picrites follow a trend of decreasing Cr at relatively constant Fe\(^{2+}\)/Ti ratio. When all Cr is consumed in crystallising liquid, phlogopite picrite spinels evolve by decreasing

**Figure 6 - Fe\(^{2+}\)/(Fe\(^{2+}\) + Mg) plotted against Al for spinels from all studied rocks.**

**Figure 7 - Fe\(^{3+}\)/(Fe\(^{3+}\) + Mg) plotted against Fe\(^{3+}\), for spinels from all studied rocks.**

Ti (ulvöspinel end-member) and increasing Fe\(^{3+}\) (magnetite end-member). All analyses of bebedouritic dyke spinels plot after this inflection towards magnetite. Wehrlite spinels appear to follow multiple evolution trends, in some respect similar to the general evolution of the dykes, but at a lower Ti level. Also, and perhaps more importantly, all wehrlitic trends start at considerably lower Cr than the phlogopite picrite trend.

This has important bearings on the petrogenetic evolution of the complex since, in the absence of extensive dunite bodies, wehrlites are the first-choice candidate among Tapira rocks to represent early cumulates, produced by fractional crystallisation of the phlogopite picrite magma. However, if this was the case, one would expect much higher Cr contents in the spinels from wehrlites. Analyses plotted in figure 10 suggest that neither phlogopite spinels nor bebedouritic dykes can be related to the wehrlites through fractional crystallisation, as far as spinel chemistry is concerned. Instead there must be Cr-rich dunites elsewhere. Perhaps these dunites are located at a lower, unexposed level of the Tapira complex. Alternatively, olivine-chromite-rich rocks could have crystallised as cumulates in a separate, fractionating magma chamber at depth. Field, petrographic, mineralogical and whole-rock geochemical evidence discussed elsewhere (Brod 1999) indicate that the second alternative is more likely to have happened. Spinels from bebedourites and carbonatites are Cr-free and plot along the Ti-Fe\(^{2+}\) side of the diagram.

Figure 11 demonstrates the two-stage evolution of Tapira spinels. Taking into account the Cr and Al variation described in previous diagrams, it can be explained in terms of initial increase in the magnetite and ulvöspinel components at the expense of Cr- and Al-spinel end-members followed, after a sharp inflection, by enrichment in the magnetite end-member at the expense of the ulvöspinel component. Note the difference between the phlogopite picrite trend and the multiple trend evolution of the wehrlite spinels. Carbonatite spinels seem to evolve in the sequence C2 to C3 to C4, becoming progressively enriched in the magnetite molecule and
depleted in Ti. Analyses of C1 spinels are not plotted, since they underwent extensive subsolidus transformation. However, the presence of ilmenite lamellae exsolved from these spinels suggests that their original Ti content was relatively high, perhaps plotting to the right of C2 spinels in the diagram. The plot for bebedourites confirms the more evolved character of B2 rocks, relative to B1.

Figure 8 - Cr-Al-Fe$^{3+}$ diagram showing the evolution trends of spinels from Tapira silicate rocks.

Figure 9 - Ti-Fe$^{3+}$-Mg plot of spinels from Tapira Rocks.
DISCUSSION AND CONCLUSIONS  Spinel-group minerals show a wide compositional variation in the different Tapira rocktypes. As a rule, spinels in the least differentiated rocks (phlogopite picrites) are chromite, evolving with magma differentiation to Cr-, Al-poor and Fe³⁺, Ti-rich spinel, by progressive and simultaneous increase in the magnetite and ulvöspinel contents. When Cr and Al become unavailable, spinel evolution shifts towards pure magnetite, at the expense of the ulvöspinel component, thus becoming progressively depleted in Ti.

The observed increase in Fe³⁺/Fe²⁺+Mg with magma differentiation in the Tapira spinels is consistent with observations from other alkaline rocks and carbonatites. Gaspar & Wylie (1983) pointed out that magnetites from the Jacupiranga complex show increasing Fe³⁺/Fe²⁺+Mg with decreasing age of the host carbonatite. Iron enrichment with magmatic evolution is also observed in spinels from lamproites (Mitchell & Bergman 1991) and orogens (Mitchell 1995).

Spinels from phlogopite picrites have the highest TiO₂ (up to 16.8 wt. %), Al₂O₃ (up to 2.74 wt. %), MnO (up to 2.76 wt. %) and MgO (up to 9.95 wt. %), whilst in the SPS and in carbonatites spinels become progressively poorer in all these elements, leading to compositions close to the ideal magnetite molecule.

Origin of Tapira wehrlites  The presence of Cr-rich spinels in phlogopite picrites is in good agreement with the primitive character of the corresponding magmas (Brod 1999), when compared with other Tapira ultramafic rocks (e.g., the bebedouritic dykes). Although the spinels from Tapira wehrlites do contain Cr, they are depleted in the chromite end-member with respect to phlogopite picrite spinels. Therefore, the wehrlites are unlikely to represent cumulates produced by fractional crystallisation of phlogopite picrite magmas. On the other hand, the bebedouritic dykes represent liquids that are too evolved to fractionate olivine and Cr-rich spinel, which renders them incapable of originating the wehrlites.

One alternative for the origin of the Tapira wehrlites is that at least some of them represent accumulations of minerals fractionated from an unevolved carbonatite magma.

If an immiscible carbonate liquid was to be able to fractionate olivine and Cr-bearing spinel to produce the Tapira wehrlites, the immiscibility event must have occurred at a very early stage, for the parental magma must have been ultramafic and Cr-rich. Results from Gaspar et al. (1998) and our unpublished data on the chemistry of olivine from carbonatite complexes suggest that olivines from Tapira wehrlites have carbonatic affinity. In this case, the Tapira wehrlites would not belong to the same fractionation series as the bebedourites, as generally thought, but would be closer to carbonatite-related rocks, such as phoscorites and nelsonites.

One problem remains to be solved if the above model is to be accepted: According to Mitchell (1997), the high Ti solubility in carbonate magmas means that perovskite would be a late-stage crystallising phase in carbonatite, in contrast with its early formation in ultramafic alkaline rocks. This is difficult to reconcile with the abundant cumulus Ca-Ti perovskite contained in Tapira wehrlites, if they were to be fractionated from an unevolved carbonatite.

Pressure and temperature constraints on perovskite stability in carbonatite liquids are still poorly known, but the preliminary data of Mitchell (1997) indicate that the first perovskite to be formed in the haplocarbonatite system, at 650°C and 1 atm will be Ca- and Ti-rich, evolving, at lower temperatures toward Na- and REE-enrichment. The question, however, is not only when perovskite will start crystallising from a carbonate liquid, but also whether there will be an adequate Ti supply, since Ti is known to partition strongly to the silicate immiscible liquid.
Figure 11 - Ti-Fe\(^{3+}\) plot showing the chromite-ulvöspinel and ulvöspinel-magnetite steps of Tapira spinel evolution. Shaded area encompasses all analyses. Note the multi-stage evolution trends for wehrlite spinels.

We suggest that, if the Tapira wehrlites are cumulates derived from an immiscible carbonate liquid, this immiscibility event must have occurred from a considerably unevolved ultramafic parent (e.g. phlogopite picrite), at high temperature, in order to explain the Cr content of wehrlite spinels. Furthermore, the immiscibility must have been incomplete, so that some Si and Ti remained in the carbonatite liquid in concentrations high enough to allow the precipitation of abundant silicate minerals (olivine, pyroxene, phlogopite) and Ca-Ti-perovskite. Brod (1999) demonstrated that the Tapira magmas underwent multiple-stage carbonate-silicate immiscibility, and that evidence for immiscible carbonate appear early in the crystallisation history of phlogopite picrites. The experimental results of Lee & Wylie (1998 a,b) show that if carbonate-silicate liquid immiscibility occurs at an early stage in the evolution of a carbonated ultramafic alkaline magma, the two liquids would be compositionally closer to each other than if immiscibility occurred in a more fractionated magma, which is in good agreement with the observations above.

Magmatic evolution of bebedourites and carbonatites  Spinel from bebedourites, bebedouritic dykes, and carbonatites are virtually Cr-free, evolving along the ulvöspinel-magnetite trend. In general, spinel chemistry indicates that B2 bebedourites are more evolved than B1, and that Tapira carbonatites evolved in the sequence (C1?) to C2 to C3 to C4, which agrees with field and other mineral chemistry and whole-rock chemistry evidence (Brod 1999, Brod et al. 2001).

From B1 to B2 bebedourites, spinel evolution is marked by progressive depletion in TiO\(_2\) and MgO, coupled with an increase in total iron and in the estimated FeO content, but not necessarily in the estimated FeO content. Manganese does not vary systematically between spinels of different SPS rock groups. Carbonatite magnetites vary within a restricted range, reflecting extreme depletion in both Cr and Al, and stronger progressive depletion in Ti, when compared with the magnetites from the SPS.

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