Exsolution in Al-Cr-Fe$^{3+}$-rich spinels from the Chilas mafic-ultramafic complex, Pakistan

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ABSTRACT

The Chilas complex contains accessory and segregated spinels that display a complete range from Cr-poor pleonaste through Al-Fe$^{3+}$-rich chromite to Cr-poor magnetite. Microprobe data reveal complete ranges for the Cr/(Cr + Al) and Fe$^{3+}$/R$^{3+}$ ratios, whereas the Mg/(Mg + Fe$^{2+}$) ratio ranges from 0.7 to 0.0; the former two ratios increase as the latter decreases. Grain to grain compositional variation within a thin section is common. It is particularly drastic in tiny spinel grains and is mainly because of subsolidus reequilibration with adjacent grains of olivine, pyroxenes, and amphibole. Many samples also contain aluminum chromium spinel with blebs and lamellae of exsolved Fe$^{3+}$-rich spinel. The exsolved grains define a complete solvus, the shape of which is similar to those of other documented examples of exsolved spinels in the system (Mg-Fe$^{2+}$)Fe$^{3+}$O$_4$-(Mg-Fe$^{2+}$)Al$_2$O$_4$. Exsolution probably took place during cooling at <600 °C.

INTRODUCTION

The Chilas complex occupies the lower part of the Kohistan magmatic arc. The complex extends east to west for more than 300 km between Nanga Parbat and the Pakistan-Afghanistan border, and it attains a maximum width of 40 km (Fig. 1). It was described in considerable detail by Jan et al. (1984) and Khan et al. (1989, and other references therein). It is predominantly composed of gabbronorite (with minor anorthosite and pyroxenite layers) and subordinate hypersthene-quartz diorites, collectively termed the principal gabbronorite association (PGA) (Khan et al., 1989). These rocks contain plagioclase of andesine-labradorite composition but are devoid of olivine. Emplaced in these rocks are veins, dikes, and leucosomes (1 m$^2$ to 5 km$^2$) of the ultramafic-mafic-anorthosite (UMA) association (Jan et al., 1984). This consists of dunite, peridotite (+ pyroxenes + hornblende + plagioclase), troctolite, gabbronorite, gabbro, anorthosite, and mafic pegmatites. These commonly contain olivine and are characterized by the presence of a very calcic plagioclase ($A_{n_{54-64}}$).

Layering is locally seen in the PGA, whereas the UMA association displays many excellent sedimentary depositional features (e.g., size and mineral-graded layering, as well as rhythmic and phase layering, truncation of earlier by later layers, cross bedding, slump folding, syndepositional faulting, and brecciation).

To supplement earlier chemical analyses of mafic mineral concentrates (Jan and Howie, 1980, 1982), we have performed thousands of spot analyses on the minerals in several dozen thin sections of the Chilas complex. This paper presents new data on chromium aluminum ferric iron spinels from the complex. Analytical techniques were described in Khan et al. (1989) and Jan and Windley (1990). Total Fe was determined as FeO, and recalculation to FeO and Fe$_2$O$_3$ was carried out by assuming R$_2$O: R$_3$O stoichiometry. In this paper Mg' = 100 Mg/(Mg + Fe$^{2+}$), Cr' = 100 Cr/(Cr + Al), Fe$^{3+}$ = 100 Fe$^{3+}$/R$^{3+}$.

OXIDE PHASES IN THE CHILAS COMPLEX

Oxide phases occur in accessory amounts (1–3%) in most rocks of the complex and rarely exceed 5%. A feature of the accessory spinel in the UMA association is that it is invariably found in very tiny grains interstitially and as inclusions in the silicate phases. The UMA association contains chromium spinel as streaks and thin layers (mostly <3 cm) and lenses less than half a meter across. No chromite segregations of commercial interest have been found in the complex.

The Chilas oxides are variable in composition like those of the plutonic rocks and xenoliths in the Lesser Antilles (especially Grenada) and Aleutian island arcs (Arculus, 1978; Arculus and Wills, 1980; Conrad and Kay, 1984; DeBari et al., 1987). The PGA contains magnetite-ilmenite pairs but no aluminum chromium spinels. The UMA association, on the other hand, contains a variety of the spinel group minerals: (1) aluminum chromium ferric iron spinel in segregations, as an accessory mineral in peridotites, troctolites, and gabbroic rocks, and rarely in anorthosites, (2) ilmenite + magnetite accompanying the chromium aluminum spinel in a few cases, and (3) pleonaste (Mg' 41–70), typically depleted in Cr and Fe$^{2+}$, in orthopyroxene-hornblende coronas resulting from olivine–calcic plagioclase reaction. In the following we pre-
sent microprobe analytical data on the aluminum chromium ferric iron spinels only. From here on, all compositions with Fe$^{3+} > 50$ and Mg$^2+ < 20$ are referred to as magnetite.

**MINERAL CHEMISTRY OF THE SPINELS**

The Chilas spinels are characterized by a great diversity of composition. Cr$^+$ and Fe$^{3+}$ span the entire range (0–100), whereas Mg$^2+$ ranges from 70 to 0. Plots of the analyses (not presented here) show that the former two increase as the latter decreases. Chemical heterogeneity is found in different samples with different mineral content. Within the limits of a thin section there may be substantial variations, especially in the tiny grains of the accessory spinel. In summary three types of variation have been observed:

**Exsolution**

Aluminum chromium spinel with blebs, lamellae, and rods of exsolved magnetite can be identified at high magnification (Fig. 2). In some thin sections the exsolved magnetite occurs in distinct grains either along edges or along fractures in the spinel grains. In one unusual chromitite, greenish brown chromite grains contain trails of exsolved blebs that are identical in composition to the magnetite occupying the interstices of the chromite grains (Fig. 3). A spinel-magnetite association of this type is a typical product of exsolution during cooling or metamorphism. Many of the exsolution features in the Chilas spinels are identical to those described from the Giant Nickel mine, British Columbia (Muir and Naldrett, 1973), Fiskensaeast Complex, Greenland (Steele et al., 1977), Tugela Rand Complex, South Africa (Eales et al., 1988), and Red Lodge, Montana (Loferski and Lipin, 1983). Like the last two examples, the Chilas host and exsolved spinels also show exsolution on a very fine scale (Fig. 4), suggesting a complex exsolution history. Our microprobe analyses are, however, for the bulk compositions without considering this fine-scale exsolution, which is not discussed further in this paper.

The exsolved magnetite and host spinel vary in composition in different samples and, to a lesser extent, in different grains within a thin section (Table 1). The variation, however, is systematic and the Cr-Al-Fe$^{3+}$ plots of the analyses apparently define a complete solvus (Fig. 5). This solvus, limited by the analyzed pairs, represents half reversal of a reaction of the type $AB_{ss} = A_{ss} + B_{ss}$; evidence for full reversal is lacking. Many samples contain one spinel phase, the analyses of which fall close to the solvus. These place an upper Cr limit on the solvus at 100 Cr/R$^{3+}$ of about 40.5. Note that, as in other areas, the tie lines of the exsolved pairs are generally parallel to the Al-Fe$^{3+}$ join. The solvus resembles the 600 °C isothermal section of chromium aluminum ferric iron spinels calculated by Sack and Ghiorso (1991, their Fig. 21). But the considerable variation in the composition of the accessory spinel grains within short distances and the
presence of very fine exsolution textures within the exsolved spinels suggest that the Chilas spinels may have exsolved over a wide range of temperature. In several chromitite samples, spinels appear to be unexsolved and do not vary in composition from grain to grain. Olivine-spinel geothermometry in these chromitites suggests temperatures of 650–570 °C (Engi, 1983; Sack and Ghiorso, 1991). Since these spinels lie above the solvus in Figure 6 and since the solvus expands with falling temperature, exsolution in the Chilas spinels might have continued to considerably lower temperatures. Temperature estimates for the accessory spinel-olivine pairs were not determined because of variation in the composition of spinel, but application of Turnock and Eugster’s (1962) data suggests that exsolution may have continued to temperatures as low as 500 °C.

The Chilas solvus is very similar to the solvi constructed for exsolved, coexisting spinel-magnetite pairs from Fiskenaesset Complex, Greenland (Steele et al., 1977), Red Lodge, Montana (the coarsely exsolved type of Loferski and Lipin, 1983), Miyamori Complex, Japan (Ozawa, 1988), and Tugela Rand intrusion, South Africa (Eales et al., 1988). In all these, the miscibility gap narrows and the existing compositions approach each other as their Cr content increases. Coexisting, exsolved oxide pairs from the western Sierra Nevada (Springer, 1974), Giant Nickel mine, British Columbia (Muir and Naldrett, 1973), and Carr Boyd complex, Western Australia (Purvis et al., 1972) also plot along the Chilas solvus; however, the solvi for the pairs from Kusa, Sweden (Zakrzewski, 1989) and the finely exsolved type from Red Lodge (Loferski and Lipin, 1983) are somewhat different. Such differences are considered essentially to reflect differences in thermal histories and extent of deformation (cf. Eales et al., 1988; Frost, personal communication).

**Grain to grain variation**

This variation is less pronounced in the segregated spinel and exsolved magnetite, but is particularly extensive in tiny grains of aluminum chromium spinel in some peridotites (Fig. 7A). An important aspect of such spinels is that, despite this variation, their plots fall along or close to the solvus. This is particularly true of a layered peridotite with streaky chromite bands in which 14 analyses plot along the Cr-rich portion of the solvus (Fig. 7B). Five
Table 1. Representative microprobe analyses of aluminum chromium ferric iron spinels and amphiboles

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH889</th>
<th>CH889</th>
<th>CH889</th>
<th>CH889</th>
<th>K981</th>
<th>6143</th>
<th>K62</th>
<th>K62</th>
<th>K62</th>
<th>K62</th>
<th>K74</th>
<th>K76</th>
<th>CH889</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.32</td>
<td>0.11</td>
<td>0.42</td>
<td>0.19</td>
<td>0.37</td>
<td>0.27</td>
<td>0.22</td>
<td>0.21</td>
<td>0.00</td>
<td>0.26</td>
<td>0.21</td>
<td>0.37</td>
<td>43.35</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.11</td>
<td>0.14</td>
<td>0.78</td>
<td>1.33</td>
<td>4.24</td>
<td>0.95</td>
<td>1.65</td>
<td>0.00</td>
<td>0.05</td>
<td>0.21</td>
<td>0.21</td>
<td>0.04</td>
<td>1.38</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.05</td>
<td>41.83</td>
<td>0.20</td>
<td>23.80</td>
<td>6.13</td>
<td>16.94</td>
<td>11.07</td>
<td>51.33</td>
<td>0.71</td>
<td>34.59</td>
<td>60.11</td>
<td>1.74</td>
<td>14.29</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>14.49</td>
<td>17.44</td>
<td>22.93</td>
<td>28.60</td>
<td>21.62</td>
<td>36.99</td>
<td>31.09</td>
<td>10.07</td>
<td>8.12</td>
<td>21.27</td>
<td>37.59</td>
<td>0.06</td>
<td>23.83</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>45.55</td>
<td>7.09</td>
<td>17.67</td>
<td>15.40</td>
<td>31.80</td>
<td>14.30</td>
<td>25.24</td>
<td>4.78</td>
<td>75.90</td>
<td>8.99</td>
<td>2.14</td>
<td>42.68</td>
<td>3.31</td>
</tr>
<tr>
<td>FeO</td>
<td>29.65</td>
<td>23.42</td>
<td>34.04</td>
<td>32.60</td>
<td>21.32</td>
<td>20.91</td>
<td>26.01</td>
<td>17.64</td>
<td>27.16</td>
<td>24.09</td>
<td>16.92</td>
<td>29.40</td>
<td>3.91</td>
</tr>
<tr>
<td>MnO</td>
<td>0.35</td>
<td>0.33</td>
<td>0.60</td>
<td>0.14</td>
<td>0.62</td>
<td>0.57</td>
<td>0.17</td>
<td>0.28</td>
<td>0.03</td>
<td>0.16</td>
<td>0.16</td>
<td>0.39</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>1.14</td>
<td>9.57</td>
<td>3.06</td>
<td>6.05</td>
<td>3.09</td>
<td>8.39</td>
<td>5.16</td>
<td>14.49</td>
<td>2.04</td>
<td>8.62</td>
<td>16.28</td>
<td>1.41</td>
<td>16.79</td>
</tr>
<tr>
<td>NiO</td>
<td>0.43</td>
<td>0.28</td>
<td>0.06</td>
<td>0.00</td>
<td>0.03</td>
<td>0.17</td>
<td>0.28</td>
<td>0.35</td>
<td>0.01</td>
<td>0.16</td>
<td>0.20</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>0.37</td>
<td>0.36</td>
<td>0.60</td>
<td>0.14</td>
<td>0.62</td>
<td>0.57</td>
<td>0.17</td>
<td>0.28</td>
<td>0.03</td>
<td>0.16</td>
<td>0.16</td>
<td>0.39</td>
<td>0.14</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Note: Analyses 1-12 are spinels, whereas 13 and 14 are amphiboles. H = host; E = exsolved. Average analyses are indicated by numbers in parentheses. CH889 = chromite layered peridotite; 1, 2, 3 from the peridotite layer; 4 and 5 from a chromitite streak. K981 and 6143 = chromitites. K62 and K76 = peridotites. K74 = dunite. Analysis 13 = amphibole away from spinel grains; analysis 14 = amphibole adjacent to a spinel grain. This contains 0.05 wt% K₂O, giving 0.01 in formula.

The variation in the spinels is most likely the result of reaction with adjacent silicate grains. Composition profiles in pyroxenes, hornblende, and olivine support this conclusion and suggest diffusion of Cr to the silicates. Some discrete spinel grains that probably were situated...
and Cr and decreases with Al. It shows an increase with Fe$^{3+}$ in spinels containing magnetite component $<40\%$, and it decreases in those containing higher magnetite contents. These observations suggest that there is Mn$^{2+}$-Fe$^{2+}$ substitution rather than Mn$^{3+}$ substitution for Cr or Fe$^{3+}$ or both.

**Discussion and conclusion**

The Chilas complex contains a variety of oxide phases. The chromium aluminum ferric iron oxides display a complete range in composition from Cr-poor pleonaste to Cr-poor magnetite through chrome with a maximum of 39 wt% Cr$_2$O$_3$. In many thin sections initially homogeneous spinel has systematically exsolved to aluminum chromium spinel host and a magnetite guest, and these pairs define a complete solvus in the system (MgFe$^{2+}$)$_{10}$Cr$_{2}$O$_{18}$-(MgFe$^{2+}$)$_{10}$Cr$_{2}$O$_{18}$Al$_2$O$_3$. This solvus is similar to those documented, albeit rarely, elsewhere. The Chilas spinels also show considerable variation from sample to sample, in thin adjacent layers of different modal mineral content, and from grain to grain within a thin section. The grain to grain variation is less pronounced in chromitites than in peridotites, in some of which it is extensive. This variation was most likely caused by reequilibration with adjacent silicates during cooling.

With the possible exception of the Miyamori Complex, all the examples of exsolved, coexisting spinel-magnetite pairs referred to in this paper occur in rocks that have undergone medium- to high-grade metamorphism. Thermobarometric calculations of coexisting pyroxenes and other phases suggest that silicates in the Chilas complex finally equilibrated at $\sim 800 \, ^\circ$C, 5-7.5 kbar. Whether these estimates suggest granulite-facies prograde metamorphism (cf. Jan and Howie, 1980) or blocking temperatures during cooling of an immense igneous body can be debated. Nevertheless, a comparison with the experimental data of Turnock and Eugster (1962) suggests that the Chilas spinels may have exsolved over a wide range of temperatures from $>700 \, ^\circ$C to as low as 500 $^\circ$C or even less. A temperature range of 650-570 $^\circ$C is independently suggested by application of the chromium spinel-olivine geothermometer of Engi (1983) and Sack and Ghiorso (1991) to a few chromitites that contain homogeneous spinel. A similar cooling range ($>800$ to $<600 \, ^\circ$C) was suggested for the Fiskensæset and Miyamori Complexes (Steele et al., 1977; Ozawa, 1983). We conclude that slow cooling from magmatic or granulate facies temperatures led to exsolution of the originally homogeneous spinels, presumably in several stages over a wide range of temperature.

Several workers (e.g., Irvine, 1967; Thayer, 1970; Ozawa, 1983) have suggested that spinel compositions can be used as petrogenetic indicators. Dick and Bullen (1984) classified spinels into different tectonic settings on the basis of Cr$^3$. Because of the likely subsolidus compositional changes, we are cautious about using the Chilas spinels for petrogenetic and petrotectonic purposes. Nev-
ertheless, an overwhelming majority of the analyses (ac-
accessory as well as segregated) have Cr' below 60 (with
the exception of the exsolved magnetite), and this groups
them with type I complexes of Dick and Bullen (1984),
which originated in midocean ridges or back-arc basins.
However, the remarkably complete ranges (0-100) of Cr' and
Fe^{3+} in the Chilas spinels are similar to those of island
arc rocks in the Lesser Antilles and Aleutian Islands (Ar-
culus, 1978; Arculus and Wills, 1980; Conrad and Kay,
1984; DeBari et al., 1987). An island arc origin of the
Chilas complex is already established on the basis of its
close association, in space and time, with arc-related rocks,
silicate composition, and whole-rock geochemistry (Jan

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