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Cr–V OXIDES FROM THE RAMPURA AGUCHA Pb–Zn–(Ag) DEPOSIT, RAJASTHAN, INDIA

WOLFRAM HÖLLER AND EUGEN F. STUMPFL

Institute of Geological Sciences, Mining University Leoben, Peter-Tunner-Strasse 5, 8700 Leoben, Austria

ABSTRACT

Two new compositional varieties of rare oxide minerals have been studied by ore microscopy and electron-microprobe analysis in samples from the high-grade metamorphic, stratiform Rampura Agucha Pb–Zn–(Ag) deposit, Rajasthan, India. We have established the presence of a Cr–V–Fe spinel and a Cr–V rhombohedral oxide. The compositions of the two minerals, $V_{0.8-1.15}Cr_{0.84-1.15}Fe_{0.6-0.67}Mn_{0.12-0.19}Mg_{0.14-0.21}Zn_{0.05-0.07}O_4$ and $V_{1.15-1.63}Cr_{0.36-0.8}Fe_{0.02-0.17}O_3$, respectively, differ from known end-members because of considerable substitution of Cr for V. Similar solid-solution series of spinels in the system $FeCr_2O_4 - FeV_2O_4 - MnCr_2O_4 - MnV_2O_4$, such as manganochromite, vuorelainenite and coulsonite, as well as relatively pure karelianite and eskolaite, have been reported from several high-grade metamorphic deposits and areas. The rare V-oxide schreyerite, $V_2Ti_3O_9$, also occurs as exsolution lamellae in rutile at Rampura Agucha. These unusual compositions are attributed to locally high concentrations of V in the precursor sediments; they further underscore the isochemical nature of regional metamorphism of the orebody.

Keywords: coulsonite, manganochromite, vuorelainenite, rutile, eskolaite, karelianite, schreyerite, Cr–V spinel, Rampura Agucha, Rajasthan, India.

SOMMAIRE

Deux groupes d'oxydes rares ont été mis en évidence au cours de notre étude pétrographique et nos analyses par microsonde électronique d'échantillons de roches fortement métamorphisées du gisement stratiforme à Pb–Zn–(Ag) de Rampura Agucha, au Rajasthan, en Inde. Il s'agit d'un spinelle à Cr–V–Fe et d'un oxyde rhomboédrique de Cr–V. La composition des deux minéraux, $V_{0.8-1.15}Cr_{0.84-1.15}Fe_{0.6-0.67}Mn_{0.12-0.19}Mg_{0.14-0.21}Zn_{0.05-0.07}O_4$ et $V_{1.15-1.63}Cr_{0.36-0.8}Fe_{0.02-0.17}O_3$, respectivement, diffère de celle des pôles à cause de la substitution considérable du Cr pour le V. Des solutions solides dans le système de spinelle $FeCr_2O_4 - FeV_2O_4 - MnCr_2O_4 - MnV_2O_4$, impliquant donc manganochromite, vuorelainenite et coulsonite, ainsi que des exemples relativement purs de karelianite et d'eskolaïte, ont été signalés dans plusieurs gisements partageant le même contexte métamorphique. La schreyerite, $V_2Ti_3O_9$, est présente sous forme de lamelles d'exsolution dans la rutile. Ces compositions assez inhabituelles résulteraient des teneurs élevées en V des sédiments précurseurs. Elles soulignent le caractère essentiellement isochimique du métamorphisme régional qui a affecté ces roches.

(Traduit par la Rédaction)

Mots-clés: coulsonite, manganochromite, vuorelainenite, rutile, eskolaïte, karélianite, schreyerite, spinelle à Cr–V, Rampura Agucha, Rajasthan, Inde.

INTRODUCTION AND GEOLOGICAL SETTING

The Proterozoic Aravalli–Delhi belt in central Rajasthan, India, hosts a large number of stratabound deposits of base-metal sulfide that are of considerable economic significance. The stratiform, sediment-hosted Rampura Agucha Pb–Zn–(Ag) deposit is located in volcano-sedimentary rocks of the Bhilwara belt (Fig. 1) at the contact with the Archean basement ("Banded Gneissic Complex"). The Bhilwara belt, a thick pile of metasedimentary rocks, was formed by intracratonic rifting of the Archean basement around 2.0 Ga ago. The deposit was formed as a consequence of hydrothermal convection, when metals were accumulated in a trough with prolific biological activity (Deb 1992, Deb & Sarkar 1990), as confirmed by $\delta^{13}C$ values from graphite of –24 to –29‰. Pb isotope studies suggest a model age of 1.8 ± 0.04 Ga for the Rampura Agucha deposit (Deb *et al.* 1989). Around 1.5 Ga ago, parts of the Banded Gneissic Complex were thrust over the western margin of the Bhilwara belt (Deb *et al.* 1989, Sugden *et al.* 1990), which led to metamorphic conditions of the upper amphibolite facies (Deb 1992).

The deposit occurs in a doubly plunging synformal structure of elliptical shape, comprising sillimanite- and graphite-bearing mica schists within garnet –

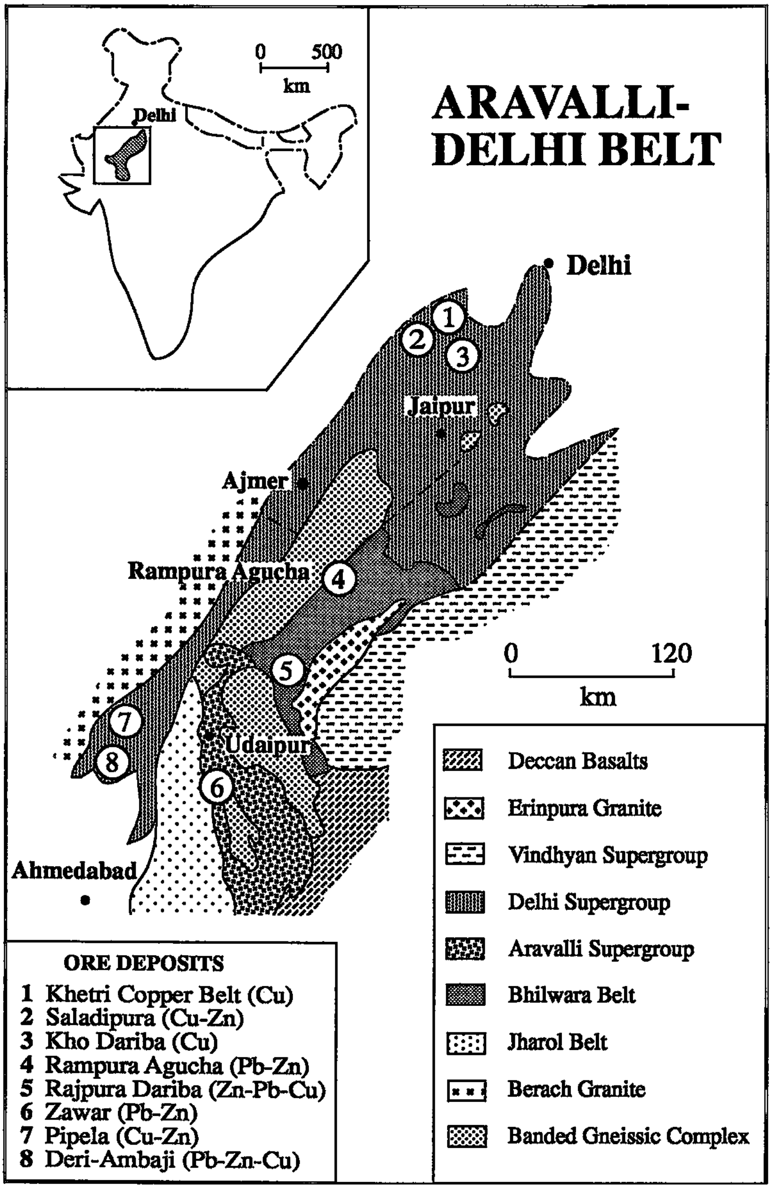

FIG. 1. Simplified geological map of the Aravalli–Delhi belt (after Sugden *et al.* 1990), including the main ore deposits. Inset map shows the location of the orogen.

biotite – sillimanite gneiss, with intercalations of amphibolite, calc-silicate rocks, and aplite. It is ideally suited for open-pit mining. The ore zone has sharp contacts with the hanging wall and footwall. The ores were metamorphosed with the host rocks under P–T conditions of the upper amphibolite facies, and have undergone polyphase deformation (Gandhi *et al.* 1984).

The general strike of the ore zone is roughly NE–SW; the dip of the orebody varies from 75° to 50° to the SE. The length of the deposit is 1550 m, the minimum depth 350 m; the width ranges from 2 to 100 m. The proven reserves are 39.2 Mt, probable reserves 13.8 Mt, and possible reserves 10.7 Mt (total 63.7 Mt) of ore (HZL Staff 1992) grading 13.6% Zn, 1.9% Pb, 9.58% Fe and 45 ppm Ag.

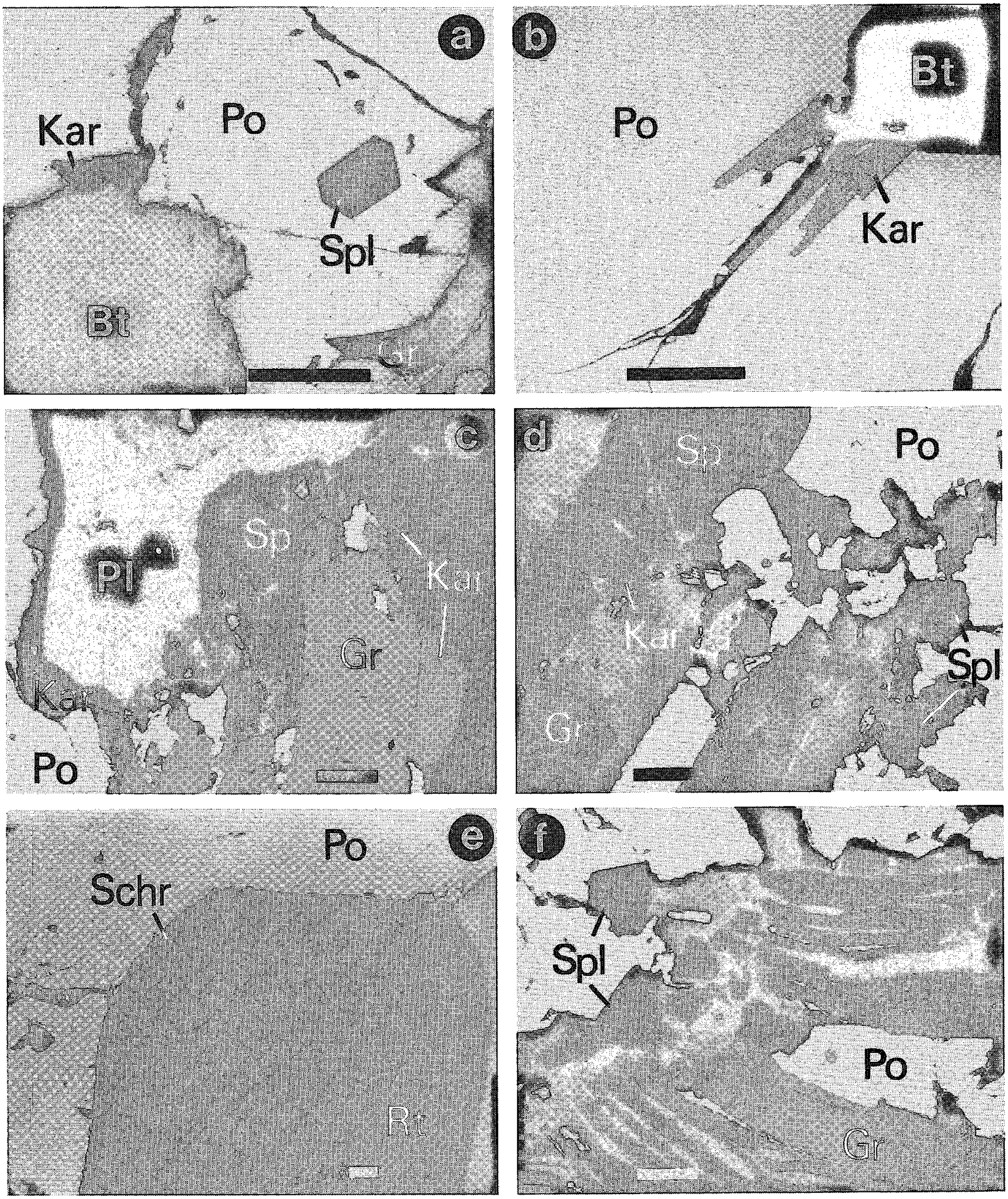

FIG. 2. (a) Euhedral crystal of Cr–V spinel (Spl) containing exsolution-induced bodies of $(Cr,V)_2O_3$ enclosed in pyrrhotite (Po) near graphite (Gr), as well as $(Cr,V)_2O_3$ (Kar) at the interface between massive pyrrhotite and biotite (Bt). (b) Prismatic crystals of $(Cr,V)_2O_3$ at the interface between massive pyrrhotite and biotite. (c) Anhedral to subhedral grains of $(Cr,V)_2O_3$ at the interface between sulfides (pyrrhotite and sphalerite) and plagioclase (Pl), as well as graphite and sphalerite (Sp). (d) Subhedral grains of Cr–V spinel and $(Cr,V)_2O_3$ between sulfides (sphalerite and pyrrhotite) and graphite. (e) Exsolution-induced lamellae of schreyerite (Schr) in rutile (Rt). (f) Euhedral to subhedral grains of Cr–V spinel, containing exsolution-induced bodies of $(Cr,V)_2O_3$, at the interface between pyrrhotite and graphite. The scale bar corresponds to 15 μm in each case.

Mineralization occurs predominantly in graphite – sillimanite – mica schist, which is enriched in V and Ni (Deb 1992). Coarse-grained sphalerite (Figs. 2c, d), by far the most widespread sulfide mineral, is associated with coarse-grained galena, granular, locally idiomorphic pyrite, and pyrrhotite in various proportions. The ore minerals carry numerous inclusions of rounded to subrounded grains of feldspar, quartz, sillimanite, muscovite, biotite and graphite. All minerals have been thoroughly recrystallized and remobilized during or after peak conditions of metamorphism. Galena is by far the most mobile of the sulfides; it exhibits ample evidence of plastic deformation and remobilization. To a lesser extent, sphalerite and pyrrhotite were remobilized during and after high-grade metamorphism. Together with Ag-sulfosalts, they fill fractures in quartz, feldspar and mica. Chalcopyrite and arsenopyrite are accessory constituents. Cr,V-bearing oxides (*e.g.*, karelianite–eskolaite solid solution; see below) are rare and have, so far, been found in five samples. Graphite is a common gangue mineral, and represents up to 10 vol.% of the bulk of average ore. It occurs as flakes in silicates or as fracture fillings and on grain boundaries (Figs. 2c, d, f). The size of the flakes, which are mostly aligned parallel to the foliation, ranges from some tens of μm to 3 mm.

The complex polymetamorphic history of the Bhilwara belt and its enclosed ore deposits has not been deciphered yet. Here, we present the first results of such investigations on the Cr–V oxide minerals; this report forms part of a comprehensive project directed at the mineralogy, geochemistry, and genesis of the Rampura-Agucha deposit.

METHODS OF INVESTIGATION

A detailed microscopic study of the ore on drill-core chip samples, representing the strike length and depth of the orebody, has been performed. After identification of the main ore and gangue minerals, the most important minor phases were analyzed with an ARL–SEMQ electron microprobe at the Institute of Geological Sciences, Leoben, using the corrections of Bence & Albee (1968). Acceleration voltage used for analyses was 15 kV at a beam current of 20 nA. Chromite (Cr, Fe, Mg, Al), willemite (Zn, Mn), ilmenite (Ti) and and metallic V were used as standards for analyses of the oxides. The atomic proportions have been calculated on the basis of four oxygen atoms (spinel), three oxygen atoms (Cr–V oxide), nine oxygen atoms (schreyerite) and two oxygen atoms (rutile). All Fe, Mn, Zn and Mg was calculated as divalent, whereas Cr, V, and Al are calculated as trivalent ions. Microprobe analyses were affected by a minor overlap of Ti*K*β and Cr*K*α, as well as Ti*K*β and V*K*α peaks. Results of analyses of minerals with high Ti contents, *e.g.*, rutile and schreyerite, have been corrected accordingly.

Owing to the small grain-size of the rare oxide minerals, it was not possible to confirm the crystal structure of spinel and karelianite–eskolaite solid-solution.

MINERALOGY

Cr–V spinel

Euhedral grains of Cr–V spinel (average size 15 μm; maximum 30 μm) occur in close association with graphite, pyrrhotite and minor sphalerite (Figs. 2a, d, f); they commonly show inclusions or exsolution-related lamellae of $(Cr,V)_2O_3$ (Figs. 2a, f). The color of the spinel in reflected light is dark grey, and very similar to that of sphalerite, with a brownish tint; the polishing hardness is obviously higher than that of the coexisting sulfides. The mineral is distinctly isotropic, without internal reflections. Reflectance values in air, measured against a calibrated chromite standard, are: 460 nm, 17.3%; 546 nm, 15.8%; 589 nm, 16.4%; 660 nm, 17.3%. These values are slightly higher than those obtained for vuorelainenite from the Sätra deposit, Sweden (Zakrzewski *et al.* 1982) and very similar to those of manganochromite from the Nairne pyrite deposit, South Australia (Graham 1978).

Electron-microprobe analyses, performed on 32 spinel grains, show considerable compositional variations. Substitution of trivalent Cr by V can be documented. V_2O_3 contents range from 26.5 to 39%, and Cr_2O_3 contents, from 29.5 to 40.3% (Fig. 3,

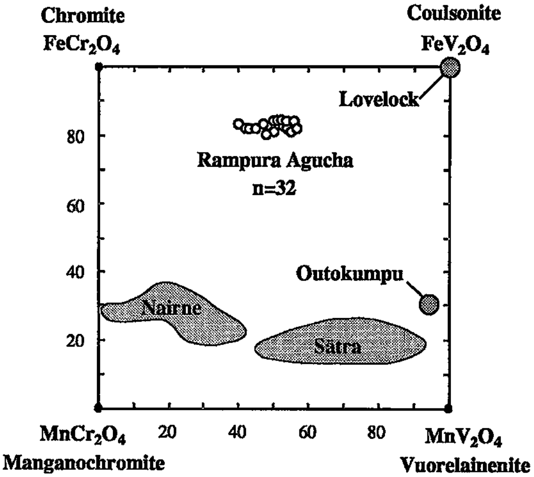

FIG. 3. Plot of compositional variations in spinel from Nairne, Sätra, Outokumpu, Lovelock and Rampura Agucha.

TABLE 1. CHEMICAL COMPOSITION OF SPINEL, KARELIANITE-ESKOLAITE SOLID SOLUTION, SCHREYERITE AND RUTILE FROM THE RAMPURA AGUCHA DEPOSIT

	Spinel			$(Cr, V)_2O_3$		Schreyerite		Rutile	
	Spl 7	Spl 34	Spl 28	Kar 2	Kar 8	Schr 4	Schr 5	Rt 8	Rt 2
V_2O_3	31,02	35,02	39,04	61,82	75,20	30,76	34,66	2,61	2,23
Cr_2O_3	38,23	33,52	30,19	38,17	23,58	4,97	4,11	0,43	0,27
Al_2O_3	0,10	0,10	0,10	n.d.	n.d.	0,34	0,36	0,10	0,10
FeO	20,28	21,93	20,79	0,84	0,76	0,65	0,80	n.d.	0,10
MnO	4,49	4,30	4,11	0,10	0,10	n.d.	n.d.	n.d.	n.d.
MgO	2,90	2,56	3,93	0,10	0,10	n.d.	0,10	n.d.	n.d.
ZnO	2,18	2,43	2,08	0,15	0,77	n.d.	n.d.	n.d.	n.d.
TiO_2	n.d.	n.d.	n.d	n.d.	n.d.	63,19	59,2'	95,99	96,06
Σwt.%	99,21	99,85	100,24	101,12	100,50	99,91	99,24	99,13	98,76
V	0,91	1,03	1,14	1,23	1,51	1,36	1.58	0,02	0,02
Cr	1,09	0,97	0,86	0,75	0,47	0,22	0,18	-	-
Al	-	-	-	-	-	0,03	0,03	-	-
Fe	0,62	0,67	0,63	0,02	0,02	0,03	0,04	-	-
Mn	0,14	0,13	0,13	-	-	-	-	-	-
Mg	0,16	0,14	0,21	-	-	-	-	-	-
Zn	0,06	0,07	0,06	-	-	-	-	-	-
Ti	-	-	-	-	-	3,26	3,17	0,98	0,98
O	4,00	4,00	4,00	3,00	3,00	9,00	9,00	2,00	2,00

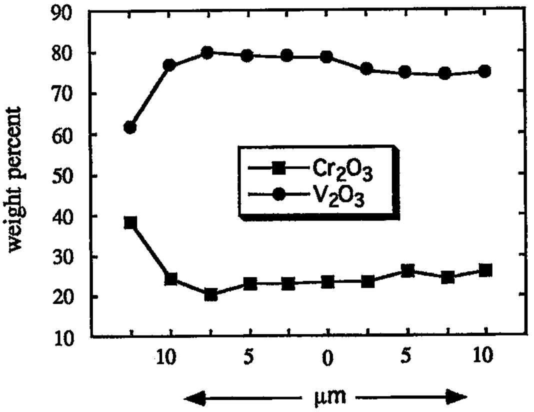

FIG. 4. Traverse across a zoned grain of karelianite–eskolaite solid solution.

Table 1). Substitutions involving the divalent cations (Fe, Mn, Mg and Zn) are less extensive than those involving the trivalent cations, with FeO from 19.8 to 21.9%, MnO from 3.8 to 4.8%, MgO from 2.4 to 3.9%, and ZnO from 1.7 to 2.4% (Table 1); These variations are not related to substitutions involving Cr and V.

Karelianite–eskolaite solid solution

Members of the solid-solution series karelianite (V_2O_3) – eskolaite (Cr_2O_3) invariably occur at or near the interface between massive pyrrhotite or sphalerite and silicate minerals (Figs. 2a, b, c) or graphite (Fig. 2d). They occur preferably as anhedral to subhedral grains (5 to 50 µm in size), but a prismatic habit commonly is developed. The crystals are mostly inclusion-free and partly intergrown with spinel (Figs. 2a, f). The color in reflected light is brownish grey, and internal reflections were not seen. In some sections, a weak but distinct anisotropism can be seen. The polishing hardness is obviously higher than that of coexisting sulfides. Despite the large differences in composition among different grains, these do not vary significantly in reflectance. Reflectance values in air, measured against a calibrated chromite standard, are: 460 nm, 20.8%; 546 nm, 21.1%; 589 nm, 22%; 660 nm, 22.2%. These values are very similar to those obtained for eskolaite (Kouvo & Vuorelainen 1958) and slightly higher than those reported for karelianite from Outokumpu (Long *et al.* 1963).

Electron-microprobe analyses of 81 grains yield a wide spectrum of compositions; few grains reveal distinct zoning (Fig. 4). There is a significant extent of replacement of trivalent Cr by V. The V_2O_3 content ranges from 58 to 81%, and the Cr_2O_3 content, from 18 to 41% (Table 1, Fig. 5). The FeO content ranges from 0.5 to 5.6%, and ZnO, from 0.1 to 0.8%, with MgO, MnO and Al_2O_3 near or below the detection limit of the electron microprobe (Table 1). There is no correlation between the Fe and Zn contents and the contents of Cr and V.

Schreyerite

Schreyerite forms fine (<5 µm) oriented exsolution lamellae (Fig. 2e) in large grains of rutile. Its color is brownish, with pleochroism from yellow-brown to grey-brown, and with strong anisotropism. Electron-microprobe analyses of schreyerite yield compositions (Table 1) similar to those obtained for schreyerite from Kwale, Kenya (Medenbach & Schmetzer 1978) and from the Sätra deposit, Sweden (Zakrzewski *et al.* 1982). Considerable Cr_2O_3 contents (up to 5%) and minor contents of Fe (<0.5% FeO) and Mg (<0.9% MgO) have been measured.

Rutile

Rutile forms rounded grains enclosed in quartz and feldspar or at contacts between sulfides and silicates. The crystals are mostly devoid of any inclusions, some contain oriented lamellae of schreyerite (Fig. 2e). Rutile contains up to 2.6% V_2O_3 and 0.4% Cr_2O_3 (Table 1), and all other elements are near or below the detection limit of the electron microprobe.

DISCUSSION AND CONCLUSIONS

(1) Cr–V oxides are commonly found in intensely metamorphosed areas and ore deposits. The Rampura-

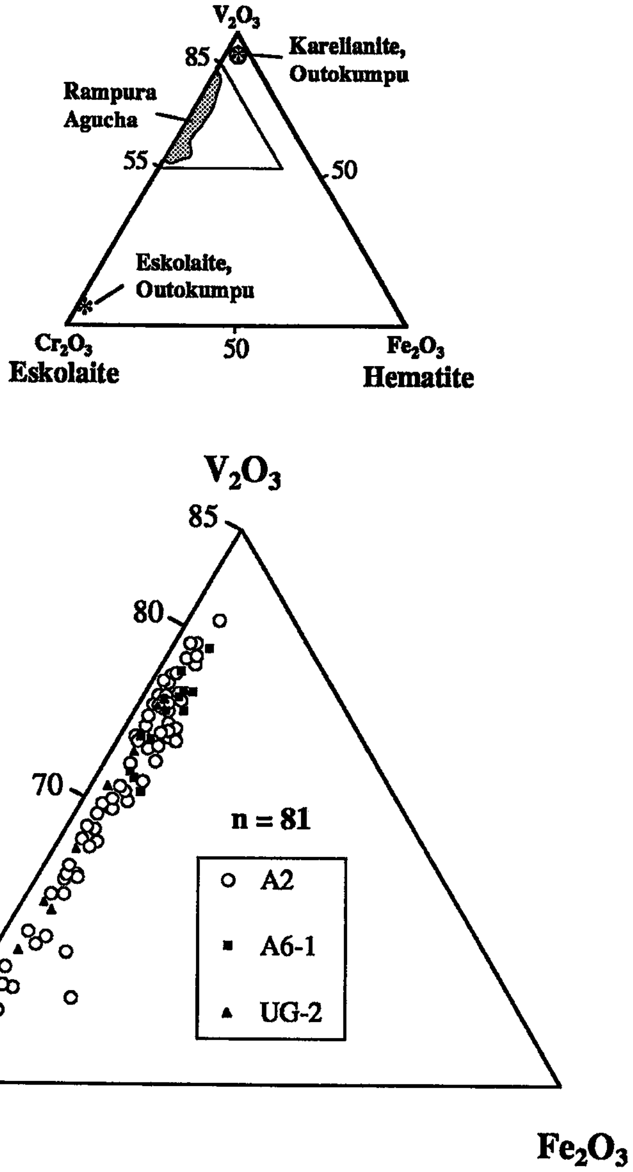

FIG. 5. Cr_2O_3–V_2O_3–Fe_2O_3 diagram showing the extent of Cr-for-V substitution in karelianite–eskolaite solid solution, with additional information concerning the karelianite (Kouvo & Vuorelainen 1958) and eskolaite from Outokumpu (Long *et al.* 1963). Sulfide and silicate assemblages of the three samples analyzed do not vary significantly. Sample A2 contains additional Cr–V spinel, and sample A6–1 contains schreyerite.

Agucha Pb–Zn–(Ag) deposit in Rajasthan, India, was metamorphosed under conditions of upper amphibolite facies and contains rare oxide minerals such as schreyerite, $(Fe,Mn)(V,Cr)_2O_4$ (spinel group) and $(V,Cr)_2O_3$ (karelianite–eskolaite solid solution). Eskolaite, Cr_2O_3 (Kouvo & Vuorelainen 1958) and karelianite V_2O_3 (Long *et al.* 1963), as well as a V, Mn-rich spinel (Long *et al.* 1963), occur in the Outokumpu orebody, Finland, which has undergone regional metamorphism with P–T conditions of 600 ± 50°C and 3.5 ± 1 kbar (Treloar 1987). Eskolaite has also been found as minute grains in a meteorite

(Kimura & Ikeda 1992). Vuorelainenite, MnV_2O_4, from the Sätra pyrite mine in Bergslagen, Sweden (Zakrzewski *et al.* 1982), and manganochromite, $MnCr_2O_4$, from the Nairne pyrite deposit, South Australia (Graham 1978), were formed during amphibolite-facies metamorphism. Coulsonite, FeV_2O_4, occurs within magnetite veins in metamorphosed igneous rock of the Buena Vista Hills, Nevada (Radtke 1962) and at the Kalgoorlie deposit, Western Australia (Spiridonov 1978), which has undergone upper greenschist metamorphism. Schreyerite, $V_2Ti_3O_9$, has been reported from a highly metamorphosed deposit of kornerupine in the Kwale district, Kenya (Medenbach & Schmetzer 1978) and from the Sätra deposit, Sweden (Zakrzewski *et al.* 1982).

(2) Cr and V are enriched in black shale (Holland 1979). Investigations on twenty deposits of black shale (Vine & Tourtelot 1970) have shown that Cr and V are preferably associated with the organic fraction. V also may be enriched in clays (Ripley *et al.* 1990), chlorite and montroseite (V,Fe)OOH (Wanty *et al.* 1990). Clays and chlorite, presumably precursor minerals in the Rampura Agucha Zn–Pb–(Ag) deposit, as well as organic matter, were consumed during prograde metamorphism to form graphite, mica and other silicate minerals. The released V and Cr may well have been used to form oxide minerals. This would be an explanation for the occurrence of Cr–V spinel and karelianite–eskolaite solid solution near interfaces involving sulfide minerals, graphite and silicate minerals. The Cr–V oxides may also have formed directly from precursor minerals like montroseite.

(3) The considerable extent of replacement of Cr by V in spinel from the Rampura Agucha deposit suggests a continuous series between the end members chromite and coulsonite (Fig. 3). Karelianite and eskolaite, noted at Outokumpu and other occurrences, are found as approximate end-member compositions. Karelianite from Outokumpu (Long *et al.* 1963) contains 3.7% Cr_2O_3, whereas eskolaite from Outokumpu (Kouvo & Vuorelainen 1958) contains 4.58% V_2O_3. Significant mutual substitution of Cr and V in $(Cr,V)_2O_3$ from Rampura Agucha deposit suggests solid solution between karelianite V_2O_3 and eskolaite Cr_2O_3 (Fig. 5).

(4) Cr and V are common trace elements in rutile. High amounts of Cr (up to 8%; Tollo & Haggerty 1987) and V (up to 1.2%; Shlyukova *et al.* 1985) are reported from the Orapa kimberlite, Botswana, and the Khibiny pluton, Russia, respectively. The present study confirms that schreyerite from the Rampura Agucha deposit has been exsolved from a previously more V-rich homogeneous titanium oxide owing to decreasing P–T conditions, as discussed by Medenbach & Schmetzer (1978).

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