

Coupled substitutions in PGE-enriched cobaltite: new evidence from the Rio Jacaré layered complex, Bahia state, Brazil

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[Received 19 November 2014; Accepted 16 February 2015; Associate Editor: B. O'Driscoll]

ABSTRACT

Microcrystals of platinum-group element (PGE)-bearing cobaltite occur in the Gulcarí A deposit of vanadiferous titanomagnetite in the lower zone of the Rio Jacaré mafic-ultramafic layered intrusion, Brazil. Aggregates of cobaltite and sperrylite are cluster-like and developed generally along the boundary of Fe-Ti oxide grains with deuteric silicates. Our observations of cryptic zoning, compositional variability and interelement correlations are based on 37 analytical points (wavelength-dispersion spectrometry mode) of cobaltite, and indicate that Ir and Rh behave uniformly with Ni and antipathetically with Co which, in turn, correlates directly with S content. Iridium, Rh and Ni apparently substitute for Co in the As-enriched grain core, and the substitution mechanism invokes solid solution with a cattierite-type molecule: $(\text{Ni} + \text{Ir} + \text{Rh}) + (\text{AsS}) = \text{Co} + (\text{S}_2)$. The PGE-bearing cobaltite probably crystallized as a primary phase at 500 to 300°C, from microvolumes of a late fluid phase. The observed enrichment in S and decrease in the As:S ratio at the cobaltite grain margins is a reflection of the increase in sulfur fugacity (f_{S_2}) with decrease in temperature of crystallization.

KEYWORDS: cobaltite–gersdorffite, platinum-group elements, zoned sulfarsenides, mechanisms of element substitution, PGE deposits, mafic-ultramafic layered complexes, Rio Jacaré, Brazil.

Introduction

THE sulfarsenides of Co and Ni are endmembers of the cobaltite–gersdorffite solid solution series, $(\text{Co}, \text{Ni})\text{AsS}$, and an important source for Co, Ni and the platinum-group elements (PGE). Cobaltite–gersdorffite associated with mafic-ultramafic rocks exhibits a wide variation in the content of PGE, especially Ir and Rh, which occur in solid solution in amounts ranging from ‘invisible’ (hundreds of ppb to ppm) to very large (>10 at.%)

PGE total), as documented in various deposits: Karik’javr (Distler and Laputina, 1979), Lukkulaivaara, Mount General’skaya, Russia (Barkov *et al.*, 1996, 1999); Las Aguilas, Argentina (Gervilla *et al.*, 1997); Yangliuping, China (Song *et al.*, 2004); Sudbury, Canada (Cabri, 1992, Szentpéteri *et al.*, 2002, Dare *et al.*, 2010); and Spotted Quoll, Australia (Prichard *et al.*, 2013).

On the other hand, genetic factors and mechanisms of compositional zoning and element substitutions in cobaltite–gersdorffite solid solutions remain not well understood. In the present paper, we examine compositional variability and zoning in microcrystals of PGE-bearing cobaltite grains from the Rio Jacaré mafic-ultramafic layered intrusion,

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DOI: 10.1180/minmag.2015.079.5.12

Brazil. We discuss genetic and crystal-chemical implications confirming the importance of coupled substitution mechanisms in Co-Ni-PGE sulfarsenides (*cf.* Barkov *et al.*, 1999, 2004).

Occurrence, specimens and electron-microprobe analysis

The Rio Jacaré layered complex, ~2.5 to 2.8 Ga in age, is a sill-like intrusion, 70 km × 1.2 km in size (Fig. 1), emplaced into folded and metamorphosed basaltic and andesitic rocks of an Archean greenstone belt (Teixeira *et al.*, 2010, and references therein). In general, the intrusion is composed of layers of olivine-bearing gabbro in the lower zone (~0.3 km in thickness), and of cumulate sequences of the upper zone (up to 1 km), subdivided into two subzones: gabbro-pyroxenite (lower) and gabbro-anorthosite (upper). The intrusion hosts world-class deposits of vanadium (V-Ti-Fe), in massive ores of titaniferous magnetite associated with zones and pods, from a few metres to 0.1 km thick. A PGE-rich mineralization is developed in association with these zones (Sá *et al.*, 2005, Campbell, 2012). Crystals of PGE-bearing cobaltite, examined in this study, are from the Gulcari A deposit, which is located in the lower zone of the complex. The Gulcari A vanadiferous titanomagnetite ore is enriched in Pt and Pd. The exotic ore mineralogy includes sperrylite, Pt-Fe-(Ni) alloys, Pd-Pt bismuthotellurides, antimonides and stannides, associated with fine-grained

magnetite-ilmenite aggregates and disseminations of interstitial base-metal sulfides, mostly chalcopyrite (e.g. Campbell, 2012).

The electron-microprobe analyses (EMPA) were conducted in wavelength-dispersion spectrometry mode (WDS) with a JEOL JXA-8200 instrument at the Bayerisches Geoinstitut, Universität Bayreuth, Germany, operated at 15 kV and 15 nA, using a finely focused beam (1 µm) and on-line correction procedures. The $L\alpha$ line was applied for Ir, Pt, Rh, Ru and As; the $M\alpha$ line for Os; the $L\beta$ line for Pd; and the $K\alpha$ line for Fe, Ni and S. Pure metals, synthetic InAs and FeS₂ were used as standards. All possible peak overlaps among the X-ray emission lines employed were checked and corrected. The present EMPA results are consistent with those obtained on related phases, using various facilities, analytical conditions and sets of standards (*cf.* Barkov *et al.*, 1999).

Results and discussion

Zoning and compositional variability

Two microcrystals of PGE-bearing cobaltite were found and analysed; one of these crystals has a diffuse core zone enriched in PGE, which is consequently brighter in contrast in BSE images (Figs 2a,b; Table 1). We used a detailed electron-microprobe traverse, made along the line AB in Fig. 2b, using automatic scanning mode with a step interval of ≤ 2 µm, in order to characterize the fine-scale compositional zoning. It appears that these data are reliable, because: (1) the grain-size of the zoned crystal is large enough, ~70 µm × 45 µm, with a homogeneous area along the path of this traverse (Fig. 2b), so that the distance from the latter to the nearest inclusions (sperrylite) is at least 5–7 µm, which is more than sufficient under the given conditions of EMPA (at 15 kV; 1-µm beam). No micro-inclusions, other than sperrylite, are present. Furthermore, the content of As in cobaltite is greater than in sperrylite; thus, in any case, the latter could not be responsible for the observed increase in As in the core (Fig. 3e). Also, minor Pt does not correlate with As (Table 1), indicating that there was no contamination by fluorescence interference during the EMPA. (2) The Ir-(Rh)-As-enriched core is observed clearly in the BSE image (Fig. 2b). The compositional variations and ranges, observed across this zone, are consistent with previous findings on related PGE-Co-Ni sulfarsenides (Barkov *et al.*, 1999).

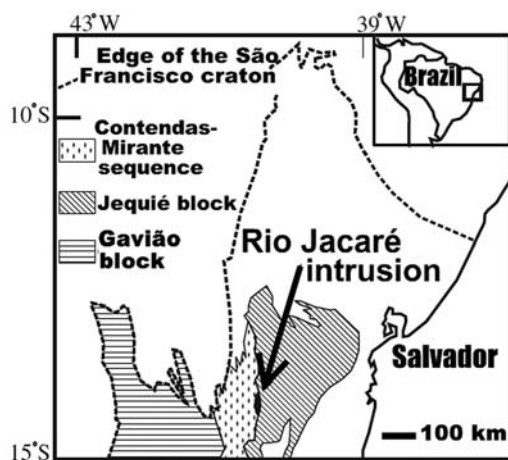


FIG. 1. Regional geology and location of the Rio Jacaré layered intrusion in Brazil (after Sá *et al.*, 2005, Teixeira *et al.*, 2010).

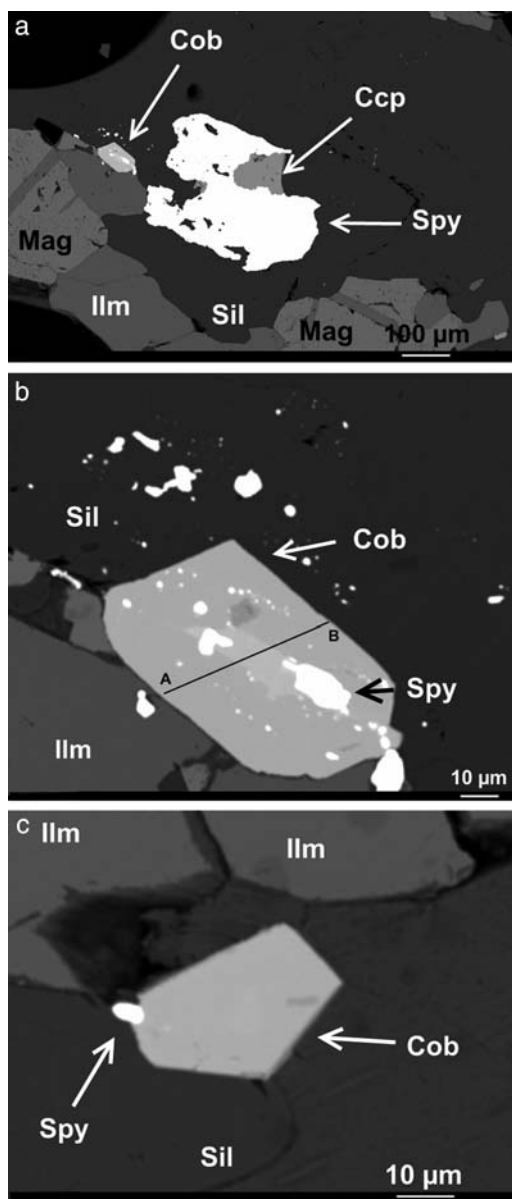


FIG. 2 (a–c). Associations and textures of grains of PGE-bearing cobaltite (Cob) and sperrylite (Spy), developed along boundary of ilmenite (Ilm) and composite grains of magnetite (Mag), containing lamellae of ilmenite, with silicate minerals (Sil). Backscattered electron (BSE) images of specimens from the Rio Jacaré layered intrusion, Brazil; Ccp is chalcopyrite (Fig. 2a). The line AB (Fig. 2b) shows the location of a detailed electron-microprobe traverse across the cryptically zoned crystal of cobaltite, containing a PGE-bearing core (diffuse and brighter in the BSE image).

Therefore, our results (Figs 3–6) reveal that the core zone is substantially poor in Co (Fig. 3a) and relatively enriched in Ni and Ir (Figs 3b,c), which display syntenic covariations with each other and with As content (Fig. 3e) and the As:S ratio (Fig. 3f). Platinum is distributed fairly heterogeneously, with occasional elevated contents (Fig. 3e). Iron tends to be relatively enriched at grain edges (Fig. 3e), but otherwise varies only slightly. Interestingly, the content of Rh is close to the minimum detection level (MDL), but a rhodium peak is observed clearly in the core of the Ir-(As)-rich zone of Fig. 3d. These results indicate that strong interrelationships exist between Ir, Rh, Ni and As (and As:S ratio). In contrast, Co covaries syntenically with S, and antipathetically with As and the metal elements.

The overall variations documented for the two analysed grains on the basis of 37 analytical points ($n = 37$) are internally consistent (Figs 4a–f). All of these compositions are notably enriched in the cobaltite endmember of the cobaltite–gersdorffite solid solution series, having >70 mol.% CoAsS (Fig. 4a). Again, Co correlates strongly with S; the correlation coefficient of linear regression, R , being 0.92 ($n = 37$; Fig. 4b). In contrast, Co is negatively correlated with As (Fig. 4c), whereas Ni is anti-correlated with S (Fig. 4d), and the Ni–As correlation is positive (Fig. 4e). As expected, As clearly substitutes for S: $R = -0.95$ (Fig. 4f).

Sperrylite associated with cobaltite (Figs 2a,b) is close to stoichiometric PtAs_2 in composition. A set of 20 WDS data points resulted in only minor-to-trace average contents of Rh (≤ 0.06), Ir (≤ 0.03) and Fe (≤ 0.1), atoms per formula unit (a.p.f.u.). A representative composition of sperrylite is Pt 55.46, Rh 0.30, Ir <0.05, Fe 0.19, S <0.01, As 43.16, total 99.11 wt.%, yielding a formula of $(\text{Pt}_{0.98}\text{Rh}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.00}\text{As}_{1.99}$, based on a total of 3 a.p.f.u.

Crystal-chemical and genetic implications

Our results (Figs 2a–f, 3a–f, 4a–f) indicate that Ir and Rh behave uniformly with Ni and antipathetically with Co which, in turn, correlates positively with S content. Presumably, Ir, Rh and Ni substitute for Co, and their incorporation in the cobaltite structure is controlled by As content. Thus, we infer the existence of a coupled mechanism of element substitutions, which involves cations and anions (or dianion groups) in order to maintain electrostatic neutrality. The effective ionic radius of S^{2-} (1.70 Å; Shannon,

TABLE 1. Representative results of electron-microprobe analyses of PGE-bearing cobaltite from the Rio Jacaré layered intrusion, Brazil.

Wt.%	µm	Co	Ni	Fe	Ir	Rh	Pt	Pd	Os	As	S	Total
1	2	28.25	1.66	3.08	0.06	0.03	0.04	0.05	<0.01	47.71	19.64	100.52
2	4	25.78	3.74	3.79	<0.01	0.01	0.37	0.05	0.13	47.69	19.15	100.70
3	6	25.91	3.55	3.77	0.31	0.02	<0.01	<0.01	<0.01	48.04	19.16	100.77
4	9	26.45	3.19	3.42	0.19	0.01	<0.01	0.02	<0.01	47.85	19.06	100.18
5	11	27.05	2.83	3.29	0.33	<0.01	0.53	0.02	<0.01	47.45	19.32	100.81
6	15	23.87	4.33	3.13	3.00	0.11	0.26	0.14	0.09	48.07	17.87	100.86
7	18	23.33	4.63	3.27	2.60	0.09	0.34	<0.01	0.38	47.73	17.72	100.10
8	20	23.38	4.54	3.35	3.07	0.04	0.53	0.03	0.11	47.79	18.04	100.87
9	24	26.49	3.01	3.24	<0.01	0.03	0.75	<0.01	0.14	47.53	19.12	100.31
10	27	27.78	2.09	3.04	0.06	0.01	0.02	<0.01	<0.01	47.43	19.33	99.76
11	30	28.53	1.68	2.89	<0.01	<0.01	0.35	<0.01	0.04	47.67	19.48	100.64
12	34	28.82	1.43	2.89	0.41	0.04	0.29	<0.01	0.13	47.15	19.63	100.79
13	39	28.31	1.56	3.40	0.15	<0.01	0.38	<0.01	<0.01	47.28	19.74	100.80
14	—	29.14	1.39	3.10	0.35	<0.01	<0.01	<0.01	0.12	46.25	19.79	100.13
15	—	28.26	2.06	3.11	0.13	0.07	0.42	0.05	<0.01	47.19	19.66	100.94
Atoms per formula unit (a.p.f.u.) based on a total of 3 a.p.f.u.												
	Co	Ni	Fe	Ir	Rh	Pt	Pd	Os	ΣM	As	S	As : S
1	0.79	0.05	0.09	0.001	—	—	0.001	—	0.93	1.05	1.01	1.04
2	0.73	0.11	0.11	—	—	0.003	0.001	0.001	0.95	1.06	0.99	1.07
3	0.73	0.10	0.11	0.003	—	—	—	—	0.95	1.06	0.99	1.07
4	0.75	0.09	0.10	0.002	—	—	—	—	0.94	1.07	0.99	1.07
5	0.76	0.08	0.10	0.003	—	0.004	—	—	0.95	1.05	1.00	1.05
6	0.69	0.13	0.10	0.027	0.002	0.002	0.002	0.001	0.95	1.10	0.95	1.15
7	0.68	0.14	0.10	0.023	0.002	0.003	—	0.003	0.95	1.10	0.95	1.15
8	0.68	0.13	0.10	0.027	0.001	0.005	—	0.001	0.95	1.09	0.96	1.13
9	0.75	0.09	0.10	—	0.001	0.006	—	0.001	0.94	1.06	1.00	1.06
10	0.79	0.06	0.09	0.001	—	—	—	—	0.94	1.06	1.01	1.05
11	0.80	0.05	0.09	—	—	0.003	—	—	0.94	1.05	1.01	1.05
12	0.81	0.04	0.09	0.004	0.001	0.002	—	0.001	0.94	1.04	1.01	1.03
13	0.79	0.04	0.10	0.001	—	0.003	—	—	0.94	1.04	1.02	1.03
14	0.82	0.04	0.09	0.003	—	—	—	0.001	0.95	1.02	1.02	1.00
15	0.79	0.06	0.09	0.001	0.001	0.004	0.001	—	0.95	1.04	1.01	1.03

These results of WDS EMP analyses (in weight %) were obtained using a JEOL JXA-8200 electron microprobe (Bayerisches Geoinstitut, Germany). No. 1–13: point analyses along the EMPA traverse AB, oriented across the cryptically zoned crystal of cobaltite with a PGE-bearing core (No. 6–8). The path of this traverse is shown in Fig. 2b; respective distances (in µm) are listed in the second column. No. 14 and 15: representative analyses of the crystal of cobaltite shown in Fig. 2c.

1976) is close to that of As^{3-} (1.78 Å; Makovicky, 2006), which should allow their mutual substitution. However, the presence of the dianion group $(\text{AsS})^{3-}$ appears more likely, consistent with the results of Wood and Strens (1979). Electronic structure calculations also suggest that the formation of the (AsS) group is favoured energetically in pyrite-type FeS_2 in order to incorporate elevated levels of As (up to 10 wt.%) under various conditions of f_{O_2} (Blanchard *et al.*, 2007). However, the structural principles of the (AsS) group present in numerous

sulfarsenide compounds are not well understood. Iron may exist as Fe^{2+} in arsenopyrite, requiring a formal valence of 2– in the associated (AsS) group (Tossell *et al.*, 1981; Ioffe *et al.*, 1985; Hem and Makovicky, 2004). The correlation of Co with S (Figs 3a,e, 4b) observed here implies a solid solution towards cattierite, the pyrite-type CoS_2 . It is known that the structural formula of pyrite-type compounds is $[\text{M}^{2+}(\text{S}_2)^{2-}]$. The maximum content of (Ir + Rh) occurs in the As-rich core (Figs 3c,e,f) of the Rio Jacaré cobaltite grains, which is clearly

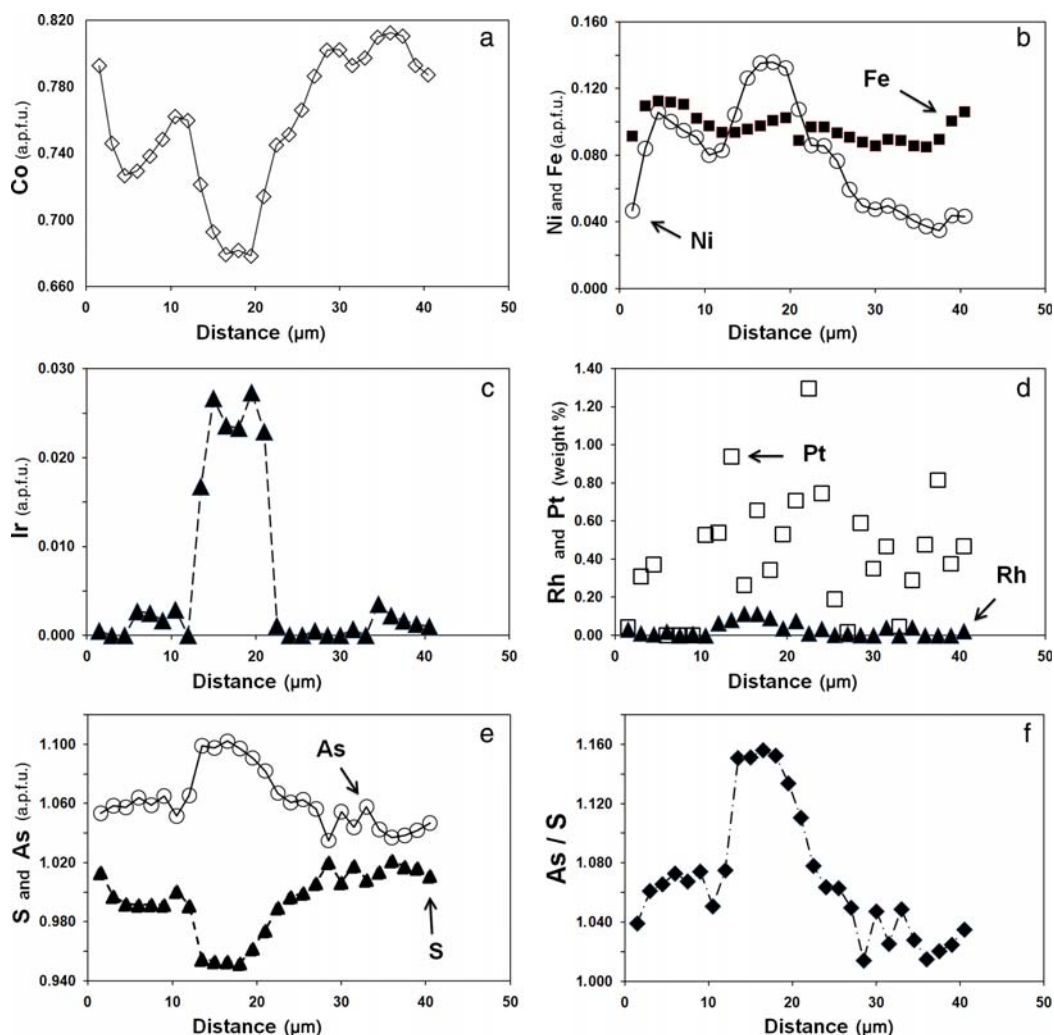


Fig. 3 (a–f). Compositional variations in contents of Co (a), Ni and Fe (b), Ir (c), Rh and Pt (d), As and S (e), expressed in a.p.f.u. (based on a total of 3 a.p.f.u.) and in values of atomic As : S ratio (f), observed along the traverse AB (shown in Fig. 2b), oriented across the zoned crystal of PGE-bearing cobaltite (Fig. 2b).

indicative of a PGE-sulfarsenide component (i.e. irarsite–hollingworthite, ideally IrAsS–RhAsS). The usual formal $3+$ valence for iridium appears likely in this case, consistent with the model of Wood and Strens (1979). The inferred exchange $\Sigma \text{M}^{3+} \leftrightarrow \text{Co}^{2+}$ is probably compensated by the involvement of dianion groups, via the following substitution: $(\text{Ni} + \text{Ir} + \text{Rh})^{3+} + (\text{AsS})^{3-} = \text{Co}^{2+} + (\text{S}_2)^{2-}$. This substitution mechanism based on the observed compositional relationships (Figs 3a–f, 4a–f) is corroborated by results on zoned PGE-rich cobaltite–gersdorffite

from the Mount General'skaya layered intrusion, sub-Arctic Russia (Barkov *et al.*, 1999).

Therefore, the present observations on cobaltite–gersdorffite from Rio Jacaré reveal that Ir and Rh are incorporated through coupled solid solution with a disulfide component (i.e. cattierite CoS_2) rather than with a metal sulfarsenide component (CoAsS or NiAsS), as might be expected. As is well known, cattierite is cubic, with $a = 5.54 \text{ \AA}$, space group $Pa\bar{3}$, and is isostructural with irarsite, IrAsS , $a = 5.78 \text{ \AA}$ and hollingworthite, RhAsS

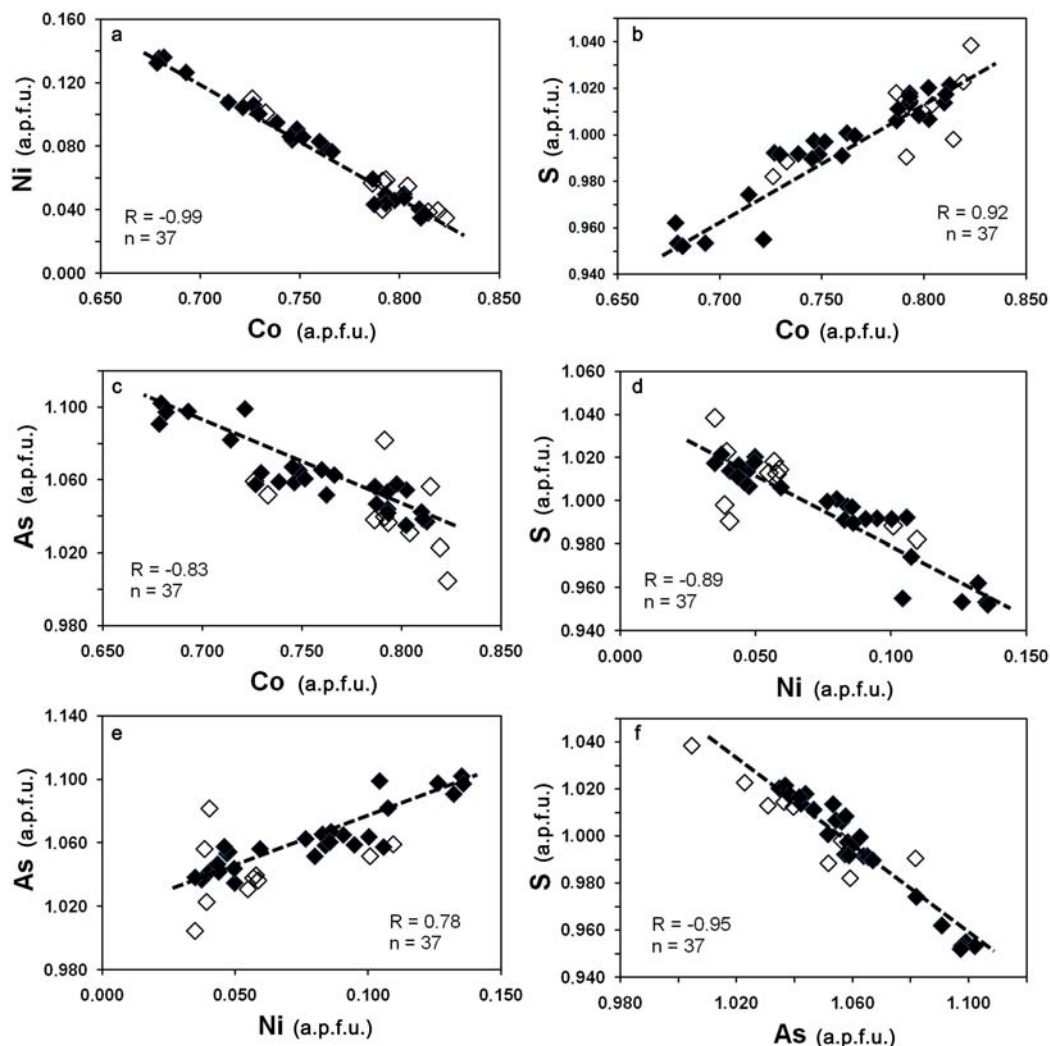


FIG. 4 (a–f). Correlation diagrams, showing Co vs. Ni (a), Co vs. S (b), Co vs. As (c), Ni vs. S (d), Ni vs. As (e) and As vs. S (f), expressed in a.p.f.u., for specimens of PGE-bearing cobaltite from the Rio Jacaré layered intrusion, Brazil. Thirty-seven data points ($n = 37$; this study) are plotted as the solid symbol for crystal one (shown in Fig. 2b) and as the open symbol for a second crystal (Fig. 2c). R is the correlation coefficient of linear regression.

(Genkin, *et al.* 1966; Pratt and Bayliss, 1979; Cabri, 2002).

In contrast, cobaltite is orthorhombic, pseudocubic, space group $Pca2_1$ (Fleet and Burns, 1990). Nevertheless, cobaltite–gersdorffite and cattierite do form extensive solid-solutions (Hem and Makovicky, 2004; Hem, 2006). Thus, the PGE-cobaltite–gersdorffite–cattierite solid solution appears to have been promoted by the overall similarity of the pyrite-type isostructural

components, in spite of the different chemistry of their dianion pairs. Our observations imply the mixed-valence character of the PGE-bearing cobaltite–gersdorffite, which probably contains both (AsS) and $(S_2)^{2-}$ groups in its structure.

In Fig. 5 we compare compositions of the analysed grains of PGE-bearing cobaltite from the Rio Jacaré complex (~ 2.5 – 2.8 Ga in age) with compositional series from two other layered intrusions: Lakkulaisvaara (~ 2.4 Ga) and Mount

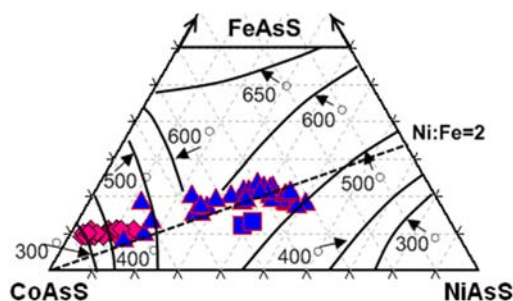


FIG. 5. Crystallization trends of PGE-bearing cobaltite–gersdorffite from layered intrusions, compared with the solvus in the system CoAsS–FeAsS–NiAsS, mol.% (Klemm, 1965). The symbols are: red diamonds, Rio Jacaré layered intrusion, Brazil (this study); blue triangles and blue squares, respectively, Mt. General'skaya (Kola Peninsula) and Lakkulaisvaara (northern Karelia) layered intrusions, Russia (Barkov *et al.*, 1996, 1999).

General'skaya (~2.5 Ga), northwestern Russia (*cf.* Barkov *et al.*, 1996, 1999). The crystallization trend extends along the line Ni:Fe = 2, consistent with an ordered distribution of Ni and Fe (Béziat *et al.*, 1996). Interestingly, our EMPA data (Fig. 6) display a good correlation between Ni:Fe and As:S ratios, confirming that mixed dianion groups are involved in the solid solutions.

In various ore deposits, a wide range of temperatures have been proposed for the crystallization of cobaltite–gersdorffite solid solutions, extending from magmatic to low-temperature hydrothermal (e.g. Szentpéteri *et al.*, 2002; Fanlo *et al.*, 2004; Dare *et al.*, 2010; Prichard *et al.*, 2013; Nimis *et al.*, 2014), which is consistent with experimental data (Klemm, 1965; Makovicky *et al.*, 1990). The compositions of

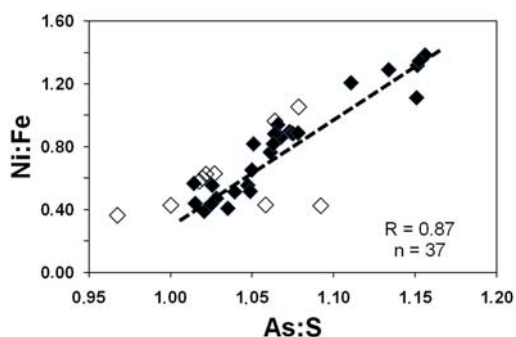


FIG. 6. Correlation of the atomic ratios Ni:Fe and As:S in PGE-bearing cobaltite from the Rio Jacaré layered intrusion, Brazil. R is the correlation coefficient of linear regression.

cobaltite at Rio Jacaré plot in a Co-rich part of the system CoAsS–NiAsS–FeAsS, similar to late zones (marginal) of zoned grains of PGE-bearing sulfarsenides from Mt. General'skaya (Barkov *et al.*, 1999), and appear to have equilibrated at 500 to 300 °C (Fig. 5). The observed textural relations are consistent with this range in temperature; the cobaltite–sperrylite aggregates are cluster-like and precipitated generally at the boundary of Fe–Ti oxides with deuteritic silicates (Figs 2a,b). Sperrylite has a similar textural relationship with Fe–Ti oxides and deuteritic silicates: it has been synthesized hydrothermally at 300 °C (Tikhomirova and Chichagov, 2000), and, indeed, is well known to have a hydrothermal association (Barkov and Fleet, 2004). We also note that the PGE-bearing cobaltite exhibits a well-developed compositional zoning, and an indication of late alteration is absent in these crystals (Figs 2b,c). Therefore, the cobaltite grains probably crystallized as primary phases, zoned from the centre to the margin, from microvolumes of a fluid phase. The observed enrichment in S content at the grain margin reflects the increase in f_{S_2} with decrease in temperature during crystallization.

Conclusions

Our observations on compositional zoning in cobaltite from Rio Jacaré indicate that Ir and Rh are probably incorporated through coupled solid solution with a disulfide component, i.e. a cattierite-type molecule CoS₂, with the involvement of dianion groups *via* the following substitution: $(\text{Ni} + \text{Ir} + \text{Rh})^{3+} + (\text{AsS})^{3-} \leftrightarrow \text{Co}^{2+} + (\text{S}_2)^{2-}$. The crystallization of the PGE-cobaltite–gersdorffite–cattierite solid solution appears to have been promoted by the overall similarity of the pyrite-type isostructural components, in spite of the existing differences in chemistry of their dianion pairs. A mixed-valence character of the PGE-bearing cobaltite–gersdorffite, which probably contains both (AsS)³⁻ and (S₂)²⁻ groups, is thus implied in its structure; the positive correlation observed between Ni:Fe and As:S ratios also suggests that mixed dianion groups are involved.

The observed zoning and compositional variations are consistent with previous results on zoned grains of PGE-rich cobaltite–gersdorffite from Mount General'skaya, sub-Arctic Russia (Barkov *et al.*, 1999). Thus, the inferred scheme of coupled substitution may well represent a type characteristic for natural solid solutions of PGE-bearing cobaltite–gersdorffite.

The microcrystals of cobaltite being studied here appear to have equilibrated at 500–300°C, and probably crystallized as primary phases, zoned from the centre to the margin, from microvolumes of a fluid under closed-system conditions. The enrichment in S content observed at the margin reflects an increase in f_{S_2} with decrease in temperature during crystallization.

Acknowledgements

The authors are grateful to Detlef Krause, Bayerisches Geoinstitut, Bayreuth University, Germany, for his expert assistance with the acquisition of the WDS EMPA data. Nigel Cook and Marian Tredoux are thanked for their reviews, and Brian O'Driscoll and Roger H. Mitchell, Principal Editor, for constructive comments. A.Y.B. thanks M.E. Fleet (University of Western Ontario) for helpful comments and D.V. Afanas'yev (rector of Cherepovets State University) for supporting research projects in Earth sciences. Y.F. and R.A.C. thank Dan MacDonald and Bob Barnett, Dalhousie University, for expert assistance with EMPA of various minerals from the Rio Jacaré complex. R.A.C. expresses a deep appreciation to 'Largo Resources Ltd.', especially to Israel Nonato, senior geologist and to Robert Anderson Campbell, Sr., for their support and encouragement. An RFBR project (16-05-00581) is acknowledged by A.Y.B.

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