

Fluoro-potassic-pargasite, $\text{KCa}_2(\text{Mg}_4\text{Al})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{F}_2$, from the Tranomaro area, Madagascar: mineral description and crystal chemistry

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[Received 5 October 2010; Accepted 24 November 2010]

ABSTRACT

Fluoro-potassic-pargasite, ideally ${}^{\text{A}}\text{K}{}^{\text{B}}\text{Ca}_2{}^{\text{C}}(\text{Mg}_4\text{Al}){}^{\text{T}}(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{F}_2$, a new amphibole species, has been found in a skarn in the Tranomaro area, Madagascar. The sample used for the description of the new mineral species is a large single amphibole crystal, 4 mm × 2 mm × 2 cm in size, brownish-black with brownish-yellow phlogopite lamellae adhering to one face of the crystal. Fluoro-potassic-pargasite is brittle, has a Mohs hardness of 6.5 and a splintery fracture; it is non-fluorescent, has perfect {110} cleavage, no observable parting, and has measured and calculated densities of 3.46 and 3.151 g cm⁻³, respectively. In plane-polarized light, it is pleochroic, X = colourless to very pale grey, Y = very pale grey, Z = colourless; $X \wedge a = 46.9^\circ$ (in β obtuse), $Y \parallel b$, $Z \wedge c = 31.4^\circ$ (in β acute). It is biaxial positive, $\alpha = 1.638(2)$, $\beta = 1.641(2)$, $\gamma = 1.653(2)$; $2V_{\text{obs}} = 49.6(4)^\circ$, $2V_{\text{calc}} = 53.4^\circ$.

Fluoro-potassic-pargasite is monoclinic, space group $C2/m$, $a = 9.9104(2)$, $b = 17.9739(4)$, $c = 5.3205(1)$ Å, $\beta = 105.534(2)^\circ$, $V = 913.11(6)$ Å³, $Z = 2$. The eight strongest lines in the X-ray powder-diffraction pattern are [d in Å(hkl)]: 3.133(100)(310), 3.270(55)(240), 2.809(47)(330), 8.413(45)(110), 2.698(39)(151), 3.374(31)(131), 2.934(29)(221) and 1.647(29)(461). Electron microprobe analysis gives SiO₂ 40.20, Al₂O₃ 17.61, TiO₂ 0.46, FeO 1.96, Fe₂O₃ 2.51, MgO 16.95, MnO 0.05, CaO 13.18, Na₂O 0.99, K₂O 3.72, F 2.75, H₂O_{calc} 0.77, sum 99.99 wt.%. The formula unit, calculated on the basis of 24 (O,OH,F) with (OH + F) = 2 - (2 × Ti), is ${}^{\text{A}}(\text{K}_{0.69}\text{Na}_{0.28}\text{Ca}_{0.04})_{\Sigma=1.01}{}^{\text{B}}\text{Ca}_{2.00}{}^{\text{C}}(\text{Mg}_{3.64}\text{Fe}_{0.24}^{2+}\text{Mn}_{0.01}\text{Al}_{0.79}\text{Fe}_{0.27}^{3+}\text{Ti}_{0.05})_{\Sigma=5.00}{}^{\text{T}}(\text{Si}_{5.80}\text{Al}_{2.20})_{\Sigma=8.00}\text{O}_{22}{}^{\text{W}}[\text{F}_{1.26}(\text{OH})_{0.74}]_{\Sigma=2.00}$. The mineral species and name have been approved by the IMA CNMNC (IMA 2009-091).

KEYWORDS: fluoro-potassic-pargasite, amphibole, new mineral, electron-microprobe analysis, optical properties, crystal-structure refinement, Madagascar.

Introduction

THE X-ray diffraction (XRD) study of a large (4 mm × 2 mm × 2 cm, Fig. 1) amphibole crystal formerly labelled as “richterite” from Tranomaro, Madagascar, in the mineralogical collection of Renato and Adriana Pagano allowed us to identify and fully characterize the K and F analogue of

pargasite, ideally $\text{NaCa}_2(\text{Mg}_4\text{Al})\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$. The end-member name derives from the nomenclature rules for minerals of the amphibole supergroup (Leake *et al.*, 2003; Burke and Leake, 2004) and the new species has been approved by the IMA CNMNC (2009-091).

Occurrence and sample description

The holotype sample of fluoro-potassic-pargasite was obtained from the mineral collection of Renato and Adriana Pagano (Cinisello, Milan,

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DOI: 10.1180/minmag.2010.074.6.961

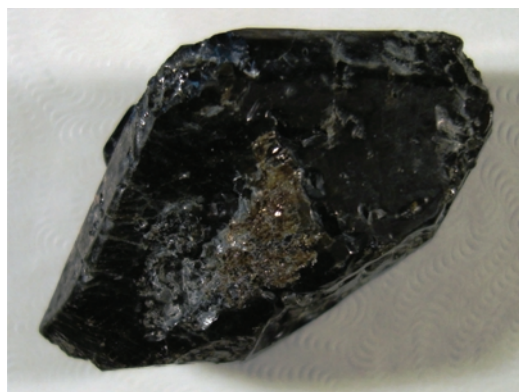


FIG. 1. The holotype specimen of fluoro-potassic-pargasite is an amphibole crystal (4 mm × 2 mm × 2 cm) with brownish yellow crystals of phlogopite adhering to the surface.

Italy), where it is specimen no. 7074B. The large crystal (Fig. 1) comes from a skarn deposit in the Tranomaro area, Fort Dauphin region, Madagascar. Moine *et al.* (1997) described two stages of metasomatism and crystallization in this area, and concluded that the amphiboles belong to

Stage 2 and were formed by alteration of diopside. The temperature and pressure conditions of metamorphism and metasomatism estimated by the same authors are $T = 850^{\circ}\text{C}$ and $P = 5$ kbar for regional metamorphism and Stage-1 metasomatism, and $T = 800^{\circ}\text{C}$ and $P = 3$ kbar for Stage-2 metasomatism. Metasomatic fluids in the Tranomaro area are generally enriched in F, promoting transport of Th, Zr and REE.

Other associated minerals reported in the skarn deposits at Tranomaro are diopside, phlogopite, apatite, calcite, anhydrite and titanite. The holotype specimen consists of a large amphibole crystal (4 mm × 2 mm × 2 cm in size) with small phlogopite crystals adhering to one face of the crystal (Fig. 1). Fragments of the holotype specimen are deposited at the Museo di Mineralogia of the Dipartimento di Scienze della Terra of the University of Pavia with the code 2009-02.

Physical and optical properties

Fluoro-potassic-pargasite is brownish-black with a vitreous lustre. It has a pale-grey streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Grains are prismatic and

TABLE 1. Chemical composition and unit formula (based on 24 anions) for fluoro-potassic-pargasite.

	Wt.%	Range of wt.%		a.p.f.u.
SiO ₂	40.20(11)	40.00–40.33	Si	5.80
TiO ₂	0.46(2)	0.42–0.48	Al	2.20
Al ₂ O ₃	17.61(8)	17.47–17.77	Sum T	8.00
FeO _{TOT}	4.22(5)	4.15–4.31	Ti ⁴⁺	0.05
FeO*	1.96		Al	0.79
Fe ₂ O ₃ *	2.51		Fe ³⁺	0.27
MnO	0.05(2)	0.02–0.07	Fe ²⁺	0.24
MgO	16.95(4)	16.89–17.01	Mg	3.64
CaO	13.18(4)	13.14–13.26	Mn	0.01
Na ₂ O	0.99(2)	0.95–1.02	Sum C	5.00
K ₂ O	3.72(2)	3.70–3.76	Ca	2.00
H ₂ O**	0.77		Sum B	2.00
F	2.75(13)	2.59–3.02	K	0.69
–O=F	–1.16		Na	0.28
Total	99.99		Ca	0.04
			Sum A	1.01
			F	1.26
			OH	0.74
			Sum W	2.00

* FeO:Fe₂O₃ ratio calculated from single-crystal Structure REFinement (SREF) results

** calculated based on 24 (O, OH, F) with (OH+F) = 2 a.p.f.u.

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TABLE 2. X-ray powder-diffraction data (strongest lines in bold typeface) for fluoro-potassic-pargasite.

I_{obs}^1	I_{SREF}^2	d_{obs} (Å)	d_{calc} (Å)	$h k l$	I_{obs}	I_{SREF}	d_{obs} (Å)	d_{calc} (Å)	$h k l$
6.9	47.6	8.963	8.986	0 2 0	4.8	51.2	2.155	2.155	2 6 1
45.1	53.5	8.413	8.432	1 1 0	5.6	6.0	2.137	2.135	$\bar{4}$ 4 1
3.9	22.3	4.922	4.929	$\bar{1}$ 1 1	2.8	37.7	2.041	2.041	$\bar{4}$ 0 2
4.5	20.3	4.491	4.493	0 4 0	15.9	24.2	2.012	2.012	3 5 1
2.4	1.6	4.212	4.216	2 2 0	7.0	10.3	1.997	1.998	3 7 0
1.9	12.0	3.981	3.982	1 1 1	5.3	10.6	1.953	1.952	1 9 0
1.3	6.8	3.892	3.895	$\bar{1}$ 3 1	27.2	15.6	1.899	1.899	5 1 0
31.1	99.5	3.374	3.374	1 3 1	5.4	6.6	1.885	1.886	$\bar{4}$ 6 1
54.7	62.1	3.270	3.272	2 4 0	9.3	14.6	1.860	1.859	2 4 2
100.0	70.9	3.133	3.134	3 1 0	4.0	8.9	1.847	1.848	$\bar{1}$ 7 2
4.5	9.6	3.056	3.057	$\bar{3}$ 1 1	6.2	4.9	1.820	1.819	5 3 0
28.8	75.9	2.934	2.934	2 2 1	3.1	8.8	1.797	1.797	0 10 0
47.2	28.7	2.809	2.811	3 3 0	2.7	8.5	1.768	1.768	$\bar{5}$ 1 2
26.2	59.0	2.754	2.755	$\bar{3}$ 3 1	7.9	15.0	1.694	1.694	$\bar{1}$ 3 3
38.8	100.0	2.698	2.698	1 5 1	7.8	11.5	1.689	1.689	$\bar{2}$ 8 2
24.6	67.4	2.586	2.586	0 6 1	6.2	13.2	1.679	1.679	$\bar{3}$ 9 1
24.2	74.0	2.561	2.563	$\bar{2}$ 0 2	28.7	36.8	1.647	1.647	4 6 1
13.3	7.5	2.414	2.415	$\bar{2}$ 6 1	4.6	10.3	1.636	1.636	4 8 0
6.0	17.8	2.383	2.383	3 5 0	6.6	15.5	1.611	1.610	1 11 0
27.2	52.7	2.345	2.343	4 2 1	7.2	4.7	1.592	1.593	3 5 2
10.3	30.2	2.298	2.296	$\bar{1}$ 7 1	11.8	29.8	1.586	1.585	$\bar{1}$ 5 3
2.9	5.8	2.249	2.250	3 3 1	3.0	3.6	1.564	1.563	$\bar{5}$ 7 1
4.6	20.5	2.225	2.226	$\bar{2}$ 4 2	17.8	26.2	1.551	1.551	$\bar{6}$ 0 2

¹ I_{obs} = relative intensities measured on a Philips PW1800 diffractometer using graphite-monochromatized Cu-K α radiation ($\lambda = 1.5418$ Å)

² I_{SREF} = relative intensities simulated from the structure-refinement results.

are defined by the {110} and {100} cleavages. Fluoro-potassic-pargasite has a Mohs hardness of 6.5; it is brittle with a splintery fracture, and has perfect {110} cleavage. The density, measured in a hydrostatic balance (using toluene instead of water), is 3.46 g cm⁻³; the calculated density is 3.151 g cm⁻³.

In transmitted light, fluoro-potassic-pargasite is pleochroic with X = colourless to very pale grey, Y = very pale grey, Z = colourless, $X \wedge a = 46.9^\circ$ (in β obtuse), $Y \parallel b$, $Z \wedge c = 31.4^\circ$ (in β acute). It is biaxial positive with indices of refraction $\alpha = 1.638(2)$, $\beta = 1.641(2)$, $\gamma = 1.653(2)$ measured with gel-filtered Na light ($\lambda = 589.9$ nm); $2V_{\text{obs}} = 49.6(3)$, $2V_{\text{calc}} = 53.4^\circ$.

Chemical composition

The fluoro-potassic-pargasite crystal used for the X-ray crystallographic study was subsequently analysed by electron microprobe using a Cameca

SX-100 operating in wavelength-dispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 μ m, peak-count time 20 s and background-count time 10 s. The following reference materials and crystals were used for K α X-ray lines: Si: wollastonite, TAP; Ti: rutile, LPET; Al: corundum (TAP); Fe: magnetite, LLiF; Mn: Mn-metal, LLiF; Mg: periclase, LTAP; Ca: wollastonite, LPET; Na: jadeite, TAP; K: orthoclase, LPET; F: fluorophlogopite syn., LTAP. Data reduction was carried out using the $\phi(\rho Z)$ 'PAP' procedure of Pouchou and Pichoir (1985). The Fe content was initially estimated as FeO; ferrous and ferric oxide proportions were calculated based on electroneutrality and crystal-chemical constraints, as described below. The average of 10 analyses is given in Table 1, together with the unit formula calculated on the basis of 24 (O,OH,F). The end-member formula is $^A K^B Ca_2^C (Mg_4 Al)^T (Si_6 Al_{12}) O_{22}^W F_2$, which requires K₂O 5.50, CaO 13.10, MgO 18.83,

TABLE 3. Miscellaneous information for fluoro-potassic-pargasite.

a (Å)	9.9104(2)	Crystal size (µm)	200 × 220 × 350
b (Å)	17.9739(4)	Radiation/monochromater	Mo- $K\alpha$ /graphite
c (Å)	5.3205(1)	Total no. of reflections	4054
β (°)	105.534(2)	No. unique reflections	2078
V (Å ³)	913.11(6)	R_{merge} %	2.60
Space group	$C2/m$	R_{obs} %	1.68
Z	2	R_{all} %	2.42
D_{calc} (g cm ⁻³)	3.151	Largest diff. peak/hole (e Å ⁻³)	0.35/−0.43

Al₂O₃ 17.87, SiO₂ 42.12, F 4.44, O=F −1.87, total 100.00 wt.%. The compatibility index is 0.002 (superior).

X-ray crystallography

Powder diffraction data

The powder-diffraction patterns were recorded using a Philips PW1800 automated powder diffractometer equipped with Cu- $K\alpha$ X-radiation ($\lambda = 1.5418$ Å). No internal standard was used. Cell dimensions refined from the experimental d values resulted in: $a = 9.911(3)$, $b = 17.972(3)$, $c = 5.322(2)$ Å, $\beta = 105.55(2)^\circ$, $V = 913.2(4)$ Å³. The indexed powder pattern is given in Table 2;

observed intensities are compared to powder-diffraction intensities simulated from the results of single-crystal structure refinement. The agreement between experimental and calculated powder diffraction intensities is not particularly good, probably because of preferred orientation in the powder-diffraction mount.

Crystal-structure refinement and crystal chemistry

A fragment removed from the holotype sample was selected for single crystal X-ray diffraction study and crystal-structure refinement based on optical properties. The data collection was carried

TABLE 4. Atomic coordinates, refined site-scattering values (ss, e.p.f.u.), atomic-displacement parameters (B_{eq} , Å²; $\beta_{\text{ii}} \times 10^4$) for fluoro-potassic-pargasite.

Atom	ss (e.p.f.u.)	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)		0.1039(1)	0.0894(1)	0.2159(2)	0.78(2)	20	8	60	−3	11	−4
O(2)		0.1188(1)	0.1740(1)	0.7368(2)	0.75(2)	17	6	72	0	4	1
O(3)	17.35(4)	0.1055(1)	0	0.7137(2)	0.86(2)	23	7	79	−	11	−
O(4)		0.3679(1)	0.2517(1)	0.7933(2)	0.91(2)	32	6	88	−1	24	0
O(5)		0.3504(1)	0.1403(1)	0.1152(2)	0.93(2)	23	8	77	0	5	7
O(6)		0.3438(1)	0.1189(1)	0.6120(2)	0.97(2)	23	8	97	1	13	−8
O(7)		0.3361(1)	0	0.2914(3)	1.24(3)	29	8	149	−	12	−
T(1)		0.2784(1)	0.0863(1)	0.3065(1)	0.50(1)	13	4	46	−1	5	0
T(2)		0.2906(1)	0.1742(1)	0.8172(1)	0.53(1)	14	5	46	0	8	1
M(1)	25.90(4)	0	0.0899(1)	½	0.63(1)	19	5	48	−	11	−
M(2)	30.06(8)	0	0.1761(1)	0	0.55(1)	15	4	50	−	8	−
M(3)	13.05(3)	0	0	0	0.60(1)	18	5	46	−	5	−
M(4)	40	0	0.2808(1)	½	0.71(1)	22	5	74	−	19	−
A	5.88(5)	0	½	0	2.85(7)	94	20	375	−	170	−
A(m)	10.35(6)	0.0269(2)	½	0.0542(5)	2.65(7)	86	17	350	−	138	−
A(2)	1.15(6)	0	0.5369(1)	0	1.75(3)						
H	0.40(6)	0.166(7)	0	0.751(13)	1.0(8)	−	−	−	−	−	−

out using a Philips PW1100 single-crystal 4-circle diffractometer equipped with graphite-monochromated Mo- $K\alpha$ X-radiation. The cell parameters were calculated from least-squares refinement of the d^* values obtained for 60 rows of the reciprocal lattice by measuring the centre of gravity of each reflection and of its antireflection in the 2θ range -70 to 70° . Unit-cell parameters are: $a = 9.9104(2)$ Å, $b = 17.9739(4)$ Å, $c = 5.3205(1)$ Å, $\beta = 105.534(2)^\circ$, $V = 913.11(6)$ Å³. The $a:b:c$ ratio obtained from diffraction data is 0.551:1:0.296. The space group is $C2/m$ as expected for calcic amphiboles.

Two monoclinic equivalents were collected in the 2θ range $4-70^\circ$, and corrections were applied for absorption and Lorentz polarization. Reflections with $I_o > 3 \sigma(I)$ were considered as observed during unweighted full-matrix least-squares refinement on F done using a program specifically written at CNR-IGG-PV to deal with

complex solid-solutions. Scattering curves for fully ionized scattering species were used at sites where chemical substitutions occur; neutral vs. ionized scattering curves were used at the T and anion sites [except O(3)]. Crystal data are summarized in Table 3. Table 4 reports the atom coordinates and the components of the anisotropic-displacement parameters, and Table 5 reports selected interatomic distances and parameters related to the conformation of the double-chain of tetrahedra. The observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine*, and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Site populations were calculated from the unit formula and validated based on the structure refinement and the methods developed for amphiboles at CNR-IGG Pavia (Table 6). In particular, the populations of the $M(1)$, $M(2)$ and

TABLE 5. Selected interatomic distances (Å) and angles ($^\circ$) in fluoro-potassic-pargasite.

$T(1)-O(1)$	1.668(1)	$T(2)-O(2)$	1.641(1)
$T(1)-O(5)$	1.695(1)	$T(2)-O(4)$	1.612(1)
$T(1)-O(6)$	1.686(2)	$T(2)-O(5)$	1.653(1)
$T(1)-O(7)$	1.663(1)	$T(2)-O(6)$	1.662(1)
$\langle T(1)-O \rangle$	1.678	$\langle T(2)-O \rangle$	1.642
$M(1)-O(1) \times 2$	2.044(1)	$M(2)-O(1) \times 2$	2.043(1)
$M(1)-O(2) \times 2$	2.113(1)	$M(2)-O(2) \times 2$	2.057(1)
$M(1)-O(3) \times 2$	2.089(1)	$M(2)-O(4) \times 2$	1.958(1)
$\langle M(1)-O \rangle$	2.082	$\langle M(2)-O \rangle$	2.019
$M(3)-O(1) \times 4$	2.081(1)	$M(4)-O(2) \times 2$	2.420(1)
$M(3)-O(3) \times 2$	2.066(2)	$M(4)-O(4) \times 2$	2.363(1)
$\langle M(3)-O \rangle$	2.076	$M(4)-O(5) \times 2$	2.604(1)
$A-O(5) \times 4$	3.069(1)	$M(4)-O(6) \times 2$	2.549(1)
$A-O(6) \times 4$	3.084(1)	$\langle M(4)-O \rangle$	2.484
$A-O(7) \times 2$	2.528(1)	$A(m)-O(5) \times 2$	3.135(1)
$\langle A-O \rangle$	2.967	$A(m)-O(5) \times 2$	3.039(1)
$O(3)-H$	0.58(1)	$A(m)-O(6) \times 2$	2.854(1)
$T(1)-O(5)-T(2)$	133.4(1)	$A(m)-O(7)$	2.539(1)
$T(1)-O(6)-T(2)$	137.2(1)	$A(m)-O(7)$	3.381(1)
$T(1)-O(7)-T(1)$	137.9(1)	$A(m)-O(7)$	2.562(1)
$O(5)-O(6)-O(5)$	163.4(1)	$\langle A(m)-O \rangle$	2.949
$O(6)-O(7)-O(6)$	103.4(1)	$A(2)-O(5) \times 2$	2.551(1)
		$A(2)-O(6) \times 2$	2.668(1)
		$A(2)-O(7) \times 2$	2.614(1)
		$\langle A(2)-O \rangle$	2.611

TABLE 6. Site populations, site scattering and mean bond lengths for fluoro-potassic-pargasite.

	Site population (a.p.f.u.)	Site scattering (e.p.f.u.)		Mean bond length (Å)	
		Refined	Calculated	Refined	Calculated
<i>T</i> (1)	2.00 Si + 2.00 Al			1.678	1.678
<i>T</i> (2)	3.80 Si + 0.20 Al			1.642	1.642
<i>M</i> (1)	1.86 Mg + 0.14 Fe ²⁺	25.90	25.96	2.082	2.065
<i>M</i> (2)	0.85 Mg + 0.04 Fe ²⁺ + 0.27 Fe ³⁺ + 0.79 Al + 0.05 Ti	30.06	29.63	2.019	2.010
<i>M</i> (3)	0.93 Mg + 0.06 Fe ²⁺ + 0.01 Mn ²⁺	13.05	12.97	2.076	2.065
Σ <i>C</i>		69.01	68.56		
<i>B</i>	2.00 Ca	40.00	40.00		
<i>A</i>	0.69 K + 0.28 Na + 0.03 Ca	17.38	16.79		
<i>X</i>	1.26 F + 0.74 OH	17.35	17.26		

M(3) sites were derived from refined site-scattering values and mean bond lengths, and those of the *T*(1) and *T*(2) sites based on the mean bond lengths and selected compositional parameters (see Oberti *et al.*, 2007, for a review).

Discussion

The only unusual feature of this sample is the large Al content of the *T* sites. ^TAl is quite ordered (Al enters the *T*(2) site only when the Si:Al ratio at the *T*(1) site is 1:1), suggesting that the temperature of crystallization is ≤800°C, as inferred by Moine *et al.* (1997). The presence of ^TAl > 2.0 a.p.f.u. and of F at the *W* position is required for the occurrence of ^ACa, which is ordered at the *A*(2) site, as found in synthetic fluoro-pargasite and fluoro-cannilloite (Oberti *et al.*, 1995; Hawthorne *et al.*, 1996). In contrast, K is ordered at the *A*(*m*) site, as expected in fluoro-amphiboles (for a review of cation ordering in amphiboles, see Oberti *et al.*, 2007; Hawthorne and Della Ventura, 2007).

Acknowledgements

The authors thank Franca Caucia (Dipartimento di Scienze della Terra, Pavia) for measuring the density. This work was supported by CNR project TA.01.004.002 and MIUR-PRIN 2007 project “Complexity in minerals: modulation, phase transition, structural disorder”, by a Canada Research Chair in Crystallography and Mineralogy, by Natural Sciences and Engineering Research Council of Canada

Discovery, Research Tools and Equipment, and Major Facilities Access grants, and by Canada Foundation for Innovation grants.

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