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Redskin Granite: a rare-metal-rich Precambrian pluton, Colorado, USA

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SUMMARY. The Precambrian Redskin stock is a high-silica alkalic granite that forms a late pluton related to the 1000 Ma-old Pikes Peak batholith. Zircon, fluorite, fluocerite, ilmenorutile, columbite, biotite, magnetite, and hematite are the most abundant accessory minerals. Thorite, monazite, and xenotime are sparse, and cassiterite and topaz very rare. The principal residences of Sn, Nb, and Ta are ilmenorutile and columbite. The occurrence of cassiterite intergrown with biotite and columbite and the high contents of Nb and Ta in cassiterite are evidence that cassiterite is also a primary mineral. The high concentrations of certain trace elements indicate a high degree of fractionation of magma prior to emplacement of the Redskin Granite. An extremely low crystallization temperature for the granite is indicated by the compositions of albite and K-feldspars, the presence of Fe-rich dioctahedral mica, the absence of Ti in magnetite, and the low content of Ti in biotite. This low crystallization temperature seems due largely to the high concentrations of F, Rb, and other volatile elements in the magma.

RECENT mineralogical and chemical studies of primary accessory heavy minerals in Tertiary igneous rocks which are hosts for molybdenite ore in Colorado (Desborough and Sharp, 1978; Desborough *et al.*, 1978) led us to study the Precambrian Redskin Granite in which cassiterite has long been known from small greisen pipes and peripheral vein systems. This granite is a late intrusive phase of the much larger Pikes Peak batholith (figs. 1, 2), which was emplaced about 1000 Ma B.P. (Barker *et al.*, 1976).

Our principal objectives were to establish the assemblage of accessory minerals in fresh, unmineralized granite; to determine the compositional variations in these elements; and to find the principal residences of Sn, Nb, Ta, Th, and rare earth elements. Sample selection was dictated chiefly by the availability of unweathered rocks at localities where greisen and fluorite veins were

absent and where the granite is megascopically homogeneous (fig. 2).

Geologic setting. The Redskin Granite is one of several small plutons intruded into the biotite granite which constitutes about 90% of the Pikes Peak batholith (fig. 1). Other late plutons include the Mt. Rosa alkalic centre (Barker *et al.*, 1975), the Lake George syenitic ring complex (Wobus and

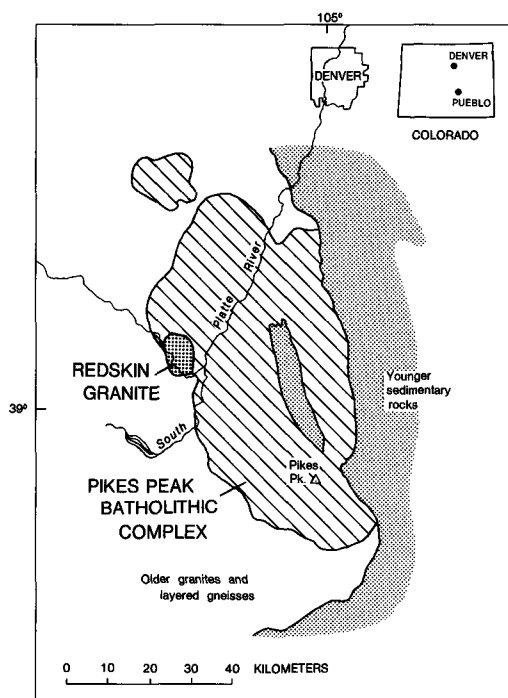


FIG. 1. Simplified geologic map of the Pikes Peak batholithic complex, Redskin Granite, and adjacent rocks.

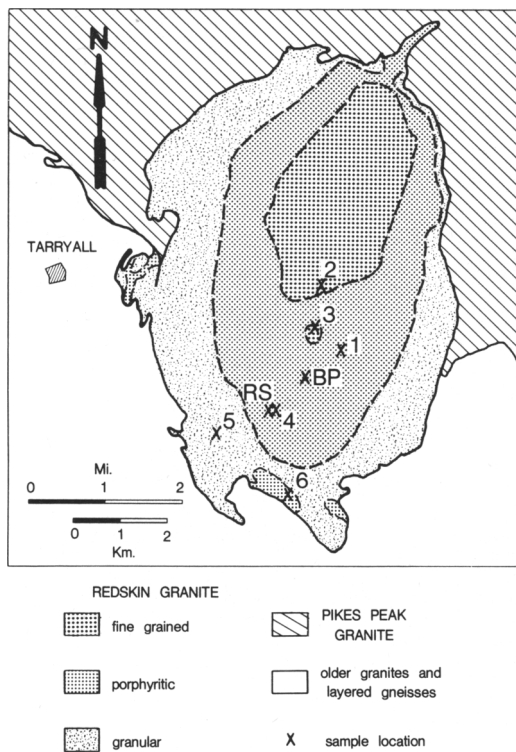


FIG. 2. Generalized map of the Redskin Granite, composed of three facies (modified from Hawley, 1969), and sample localities.

Anderson, 1978), and the Tarryall Mountains batholith (Hawley and Wobus, 1977).

Hawley (1969) and Hawley and Wobus (1977) have made extensive petrographic, modal, and chemical studies of the Redskin and surrounding rocks and the following summary is based largely on their investigations. The three major textural facies are, from oldest to youngest, granular, porphyritic, and fine-grained (fig. 2). Modally, all the rocks are granites according to Tuttle and Bowen (1958) and Streckeisen (1976). Modal variations between textural units are moderate, but systematic. From oldest to youngest, the proportions of plagioclase and muscovite increase and perthitic microcline decreases. All facies contain about 0.5% fluorite. Major element variations among the facies of the Redskin are not significant. Table III shows the average composition of the Redskin Granite and the main phase biotite granite.

A few small greisen bodies, pegmatites, and quartz veins are associated with the Redskin Granite. Greisen pipes and quartz veins extending from greisen have been prospected for cassiterite,

beryl, wolframite, molybdenite, gold, and other rare minerals, but these minerals are so sparse that there has been virtually no production (Hawley *et al.*, 1966). Small fissure veins in an adjacent area also have this assemblage, and may have supplied Sn and W minerals to small placer deposits.

The mineralogy and chemistry of the Redskin Granite is similar to that of tin granite, as defined by Tischendorf (1974). This was the reason we chose to study the mineralogy and composition of heavy accessory minerals to determine the concentration and mineralogical residence of Sn, Nb, and Ta, and to obtain new information about the composition of feldspars and micas.

Accessory minerals

Mineral separation and methods of analysis. Samples ranged from 20 to 30 kg and were crushed to minus-40 mesh. Each was separated into three fractions using bromoform ($D = 2.89$) and methylene iodide ($D = 3.32$). All samples have from 1.0–4.6 wt% of heavy minerals ($D > 2.89$). Minerals with specific gravity greater than 3.32 constitute 0.1–0.3 wt%. About 90% of the heavy minerals is biotite.

Mineral identification and determination of element residence was by electron-microprobe analysis of polished grain mounts of each heavy-mineral fraction. The relative abundance of heavy minerals was determined by identifying each of several hundred grains in each grain mount using both wavelength and energy-dispersive analysis and a multichannel analyser on the electron microprobe. These studies showed that, in order of decreasing abundance, zircon, fluorite, fluorcerite, ilmenorutile, columbite, magnetite, and hematite are the major accessory minerals. Thorite, monazite, and xenotime are less abundant, and cassiterite and topaz are very rare. A low-Nb ilmenite was found in sample 6 (Table II). Virtually all of the heavy minerals are nearly invariant in composition, except for ilmenorutile and columbite which are highly variable, and which are the major hosts for Nb, Ta, and Sn.

Ilmenorutile. Table I shows the compositional variations and intergrain inhomogeneities among ilmenorutile grains from five localities. Table II gives the mean Sn, Ta, and Nb concentrations for 18–20 ilmenorutile grains in each of five samples.

Columbite. Compositional data for columbite grains from five localities are shown in Table I. In addition to the major elements, Sc is present in all grains, ranging from 0.2 to 1.0 wt% Sc_2O_3 ; Sn may amount to 0.5 wt% of SnO_2 , but is below the detection limit in eight grains. Table II gives the Sn and Ta content for 85 grains from five localities.

Table 1. Quantitative data for certain elements in accessory ilmenorutile, columbite, and cassiterite in the Redskin Granite determined by simultaneous quantitative elemental analysis. [Mean (\bar{X}), standard deviation (σ), and detection limits for minor elements are all given in weight percent. N = number of observations per grade. Sample numbers refer to localities shown in Figure 2. < = below detection limits $\pm 3 \times \sigma$ of zero concentration.]

Ilmenorutile
[Detection limits: Nb - 0.06, Fe - 0.04, Sn - 0.2, Sc - 0.04, Ta - 0.10]

Sample localities	1			2			3			BP			RS		
	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.
Nb ₂ O ₅	7.0 (1.8)	1.9 (2.5)	<	2.4 (1.2)	5.7 (0.7)	1.3 (0.4)	2.4 (0.9)	0.9 (0.1)	2.5 (0.7)	8.8 (6.4)	6.3 (1.8)	<	4.0 (0.4)	6.1 (1.6)	4.6 (3.0)
TiO ₂	82.2 (2.8)	25.3 (4.3)	<	95.4 (1.7)	89.4 (2.8)	83.6 (0.8)	93.7 (2.0)	99.2 (1.7)	92.1 (4.2)	86.2 (7.5)	86.1 (4.2)	<	77.9 (0.8)	77.6 (2.5)	77.1 (11.1)
FeO	6.8 (0.8)	5.7 (0.5)	<	3.3 (1.3)	3.3 (0.3)	2.1 (0.9)	6.5 (0.3)	2.8 (0.6)	5.1 (1.3)	5.8 (2.6)	5.1 (1.3)	<	9.5 (0.3)	7.5 (0.8)	13.0 (7.8)
SnO ₂	3.1 (0.5)	1.6 (0.4)	<	3.9 (0.3)	3.9 (0.3)	1.5 (0.4)	1.5 (0.4)	2.2 (0.5)	2.0 (0.1)	2.0 (0.1)	0.5 (0.1)	<	0.3 (0.06)	2.3 (1.3)	0.6 (1.3)
Sc ₂ O ₃	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<
Ta ₂ O ₅	0.7 (0.2)	0.7 (0.2)	<	0.5 (0.2)	0.5 (0.2)	0.5 (0.2)	0.4 (0.1)	0.7 (0.1)	0.7 (0.6)	1.1 (0.9)	1.5 (0.6)	<	1.7 (0.1)	0.5 (0.1)	0.7 (0.2)
N	6	6	4	6	5	5	6	6	6	4	4	4	3	4	4

Columbite
[Detection limits: Ti - 0.5, Fe - 0.4, Sn - 0.1, Sc - 0.05, Ta - 0.02]

Sample localities	1			2			3			BP			RS		
	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.
Nb ₂ O ₅	50.4 (5.4)	61.2 (1.3)	<	59.8 (2.5)	54.1 (6.6)	58.3 (1.8)	76.7 (3.5)	61.9 (4.8)	60.8 (3.6)	49.2 (3.7)	52.9 (0.4)	53.1 (1.8)	47.1 (1.5)	57.2 (1.8)	54.6 (1.8)
TiO ₂	8.3 (0.5)	1.8 (0.2)	<	6.3 (0.3)	3.5 (1.0)	2.8 (0.5)	3.7 (0.7)	2.5 (0.3)	2.7 (0.3)	3.8 (0.5)	4.0 (0.5)	4.0 (0.8)	5.3 (0.2)	2.5 (0.2)	2.5 (0.3)
FeO	18.0 (0.8)	18.3 (1.4)	<	20.5 (3.0)	18.7 (0.6)	19.3 (1.9)	18.9 (1.3)	18.3 (0.6)	25.3 (5.0)	18.1 (0.8)	21.6 (3.0)	23.0 (1.2)	17.2 (0.6)	19.9 (0.6)	18.5 (1.0)
SnO ₂	0.3 (0.2)	<	<	0.1 (0.1)	0.1 (0.06)	<	0.2 (0.1)	<	<	0.3 (0.1)	0.2 (0.1)	0.4 (0.2)	0.5 (0.1)	<	<
Sc ₂ O ₃	0.4 (0.05)	0.2 (0.01)	<	0.3 (0.08)	0.3 (0.03)	0.3 (0.05)	0.3 (0.08)	0.3 (0.08)	0.3 (0.05)	0.3 (0.1)	0.3 (0.1)	0.8 (0.1)	0.7 (0.1)	0.8 (0.1)	0.3 (0.1)
Ta ₂ O ₅	23.2 (4.4)	9.6 (0.4)	<	3.2 (2.0)	18.5 (4.5)	14.9 (0.9)	13.9 (1.7)	14.5 (2.3)	16.8 (2.0)	19.0 (4.0)	18.8 (0.7)	13.4 (1.2)	15.9 (1.2)	14.2 (1.2)	14.6 (1.2)
N	5	6	5	6	6	5	5	4	6	6	3	6	2	6	6

Cassiterite
[Detection limits: Nb - 0.5, Ti - 0.3, Fe - 0.9, Sc - 0.08, Ta - 0.08]

Sample localities	BP			RS		
	\bar{X}	σ	D.L.	\bar{X}	σ	D.L.
Nb ₂ O ₅	1.6 (0.7)	3.2 (0.4)	<	3.0 (0.6)	3.0 (0.4)	0.6 (0.4)
TiO ₂	1.2 (0.3)	0.7 (0.2)	<	1.7 (0.5)	1.0 (0.3)	1.2 (0.2)
FeO	<	<	<	<	<	<
Sc ₂ O ₃	<	<	<	<	<	<
Ta ₂ O ₅	1.2 (0.7)	1.4 (0.7)	<	1.2 (1.5)	1.5 (0.6)	1.3 (0.4)
N	5	6	6	6	6	6

Table II. Concentration of tin and tantalum in columbite, and of tin, tantalum, and niobium in ilmenorutile from five samples of Redskin Granite. One observation per sample. N = no. of grains; detection limit: SnO₂ = 0.20, Nb₂O₅ = 0.15, < = below detection limit; all weight percent.]

Sample no.	Ilmenorutile			Columbite		
	\bar{X}	σ	N	\bar{X}	σ	N
1	SnO ₂ 0.6	0.9	(N = 20)	SnO ₂ 0.3	0.4	(N = 17)
	Ta ₂ O ₅ 1.0	0.6		Ta ₂ O ₅ 1.1	0.4	
	Nb ₂ O ₅ 6.6	5.1		Nb ₂ O ₅ 3.6	2.5	
2	SnO ₂ 0.2	0.6	(N = 18)	SnO ₂ 0.2	0.6	(N = 19)
	Ta ₂ O ₅ 0.4	0.2		Ta ₂ O ₅ 0.8	0.7	
	Nb ₂ O ₅ 3.3	1.9		Nb ₂ O ₅ 5.9	4.0	
3	SnO ₂ 0.3	0.4	(N = 18)	SnO ₂ 0.3	0.4	(N = 18)
	Ta ₂ O ₅ 1.1	0.4		Ta ₂ O ₅ 1.1	0.4	
	Nb ₂ O ₅ 3.6	2.5		Nb ₂ O ₅ 3.6	2.5	
4	SnO ₂ 0.6	0.9	(N = 19)	SnO ₂ 0.6	0.9	(N = 15)
	Ta ₂ O ₅ 0.8	0.7		Ta ₂ O ₅ 0.8	0.7	
	Nb ₂ O ₅ 5.9	4.0		Nb ₂ O ₅ 5.9	4.0	
6	SnO ₂ 0.1	0.1	(N = 18)	SnO ₂ 0.1	0.1	(N = 16)
	Ta ₂ O ₅ 0.2	0.2		Ta ₂ O ₅ 0.2	0.2	
	Nb ₂ O ₅ 3.6	1.8		Nb ₂ O ₅ 3.6	1.8	
6	SnO ₂ <	<		Ilmenorutile (N = 19)	<	
	Ta ₂ O ₅ <	<		Ta ₂ O ₅ <	<	
	Nb ₂ O ₅ 2.2	1.3		Nb ₂ O ₅ 2.2	1.3	

Table III. Average composition of the Redskin Granite and the main phase biotite granite of the Pikes Peak batholith.

	MAJOR ELEMENTS		TRACE ELEMENTS (ppm)		
	Redskin granite	biotite granite	Redskin granite	biotite granite	
SiO ₂	74.5	72.6	Li	105	63
Al ₂ O ₃	13.2	13.4	Be	8	5
TiO ₂	0.10	0.28	Rb	458	250
FeO*	1.5	2.5	Sr	28	120
MgO	0.05	0.14	Y	84	74
CaO	0.71	1.18	Zr	202	318
Na ₂ O	4.00	3.31	Nb	95	44
K ₂ O	4.88	5.60	Sn	16	10
P ₂ O ₅	0.01	0.05	Cs	3.7	2.8
MnO	0.04	0.07	Ba	289	916
Cl	0.01	0.01	La	71	108
F	0.46	0.35	Ce	156	227
H ₂ O(+)	0.27	0.35	Eu/Eu [#]	.25	.50
Sum	99.73	99.88	Ta	13	4
			Th	53	27
			U	7.3	4.5

* FeO is total iron reported as FeO. # Eu normalized to chondrites.

DATA SOURCES: Redskin Granite major elements, average of 13 analyses of Hawley and Wobus (1977); biotite granite major elements, average of 19 analyses of Barker and others (1975). Trace elements-Li, Be, and Sn from Hawley and others; Rb, Sr, Y, Zr, Nb, and Ba-KRF analyses, 6 samples Redskin granite, 13 samples biotite granite; Cs, La, Ce, Eu, Ta, Th, and U by INAA, 6 samples Redskin Granite, 9 samples biotite granite.

Table IV. Composition of feldspar phenocryst for the three facies of the Redskin Granite and three other rock types of the Pikes Peak batholith

Rock type	Alkali feldspar	Plagioclase
Redskin Granite		
Granular facies	Or ₇₆	An ₃
Porphyritic facies	Or ₉₀	An ₃
Fine-grained facies	Or ₉₆	An ₃
Pikes Peak batholith (Barker and others, 1975)		
Quartz syenite	Or ₃₈	An ₆
Fayalite granite	Or ₄₀₋₆₅	An ₈
Biotite granite	Or ₆₂	An ₆

Table V. Microprobe analyses of micas. [ph = white mica, bi = biotite, (n) = number of analyses, σ = standard deviation in percent.]

Sample No.	1		2		3		4		5		6		σ(%)			
	ph	n	ph	n	ph	bi	ph	bi	bi	bi	bi	bi				
SiO ₂	48.4	(12)	48.2	(9)	48.9	(5)	35.8	(9)	48.9	(15)	35.0	(21)	35.2	(34)	37.4	3
Al ₂ O ₃	29.6		28.4		29.7		18.7		27.1		17.9		17.3		19.5	3
TiO ₂	0.37		0.48		0.81		1.9		0.31		1.8		2.2		1.7	7
FeO*	9.3		8.3		7.2		27.3		9.1		26.1		28.8		26.5	4
MnO	0.30		0.07		0.26		0.78		0.31		0.82		0.69		0.74	9
MgO	0.55		1.6		0.89		1.2		0.87		0.97		0.46		0.42	3
K ₂ O	10.3		9.9		10.3		9.8		10.1		9.6		9.5		9.8	2
Cl	0.02		0.05		0.08		0.13		0.02		0.19		0.20		0.10	10
F	1.3		1.9		2.3		2.0		2.8		2.8		1.4		2.0	10
Sum	100.14		98.90		100.44		97.61		99.51		95.18		95.75		98.16	
-O = F,Cl	.55		.81		.99		.87		1.18		1.22		.63		.86	
Sum	99.59		98.09		99.45		96.74		98.33		93.96		95.12		97.30	
Number of ions on the basis of 22 positive charges																
Si	3.21	4.00	3.24	4.00	3.23	4.00	2.78	4.00	3.31	4.00	2.81	4.00	2.80	4.00	2.86	4.00
Al	0.79		0.76		0.77		1.22		0.69		1.19		1.20		1.14	
Al	1.52		1.49		1.55		0.49		1.47		0.51		0.42		0.61	
Ti ⁺²	0.02		0.02		0.04		0.11		0.02		0.11		0.13		0.10	
Fe	0.52	2.13	0.47	2.15	0.40	2.10	1.78	2.57	0.51	2.11	1.76	2.56	1.91	2.56	1.70	2.56
Mn	0.02		0.01		0.02		0.05		0.02		0.06		0.05		0.05	
Mg	0.05		0.16		0.09		0.14		0.09		0.12		0.05		0.05	
K	0.87		0.85		0.87		0.97		0.87		0.99		0.97		0.95	
Cl	tr		tr		0.01		0.02		tr		0.03		0.03		0.01	
F	0.26	2.00	0.41	2.00	0.48	2.00	0.49	2.00	0.60	2.00	0.70	2.00	0.34	2.00	0.48	2.00
OH+	1.74		1.59		1.51		1.49		1.40		1.27		1.63		1.51	

*Total iron reported as FeO

+Calculated

Fig. 3 shows photomicrographs of columbite grains in association with cassiterite and biotite.

Cassiterite. Only a few grains of cassiterite were found among several thousand heavy-mineral grains. One $10 \times 20 \mu\text{m}$ grain was noted as an inclusion in K-feldspar in one light-mineral fraction. The larger cassiterite grains ($100 \times 300 \mu\text{m}$) occur in contact with columbite and biotite (fig. 3A, B, C). The minor elements analysed in seven cassiterite grains are given in Table I. Nb, Ti, and Ta are the most abundant minor constituents, and all of these average 0.6 wt% or more of the respective oxides.

Trace elements

Ludington *et al.* (1979) presented concentration data for twenty-eight elements in samples 1-6 and compared them to the main phase biotite granite of the Pikes Peak batholith and significant contrasts were recognized. The average concentration of trace elements for these two rock types are shown in Table III. Notable features of the Redskin Granite include: $\text{K/Rb} < 100$, $\text{Rb/Sr} > 10$, and $\text{Zr/Nb} < 3$. Concentrations of Sn, Nb, and Ta are three to five times those of average low-Ca granite given by Turekian and Wedepohl (1961).

Composition of feldspars and micas

Feldspars. Hawley and Wobus (1977) have shown that all intrusive phases of the Redskin are subsolvus granites, with almost equal amounts of potassium and sodic plagioclase feldspars. Though they lacked precise data on feldspar composition they suggested that because of the presence of two alkali feldspars, the Redskin Granite 'must have crystallized below a temperature range of 640-80 °C, and perhaps much below this'.

We attempted to measure the initial composition of alkali feldspar and plagioclase phenocrysts as follows: microprobe analysis of thirty-four spots in plagioclase phenocrysts from all samples ranged from between An_1 to An_5 . An additional thirty-three spots in albite exsolved from alkali feldspar phenocrysts yielded a range from An_4 to An_0 . In both types of albite, compositional variations between spots were greater than between grains, samples, or intrusive phases. Analysis of forty-seven spots in potassium feldspar exsolved from alkali feldspar phenocrysts ranged from Or_{96} to Or_{100} . No significant variation between samples or intrusive phases was noted.

The composition of plagioclase phenocrysts were taken to represent initial compositions because of the lack of any calcic reaction products and the low calcium content of the rocks, which is largely

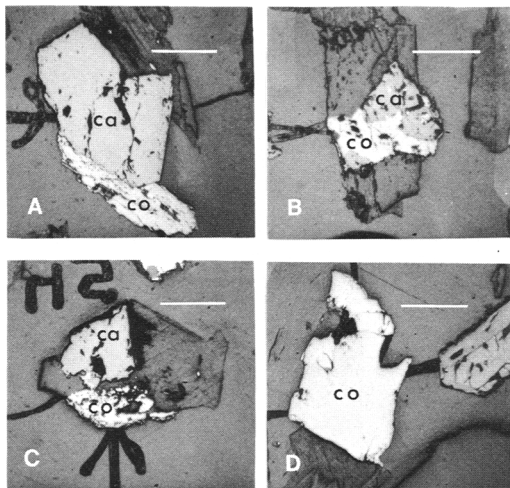


FIG. 3. Reflected light photomicrographs of cassiterite (ca) and columbite (co) in grain mounts of heavy-mineral concentrates of samples BP and RS. White bar scale is $100 \mu\text{m}$. A, Subhedral cassiterite attached to columbite and biotite, Sample BP. B, Cassiterite intergrown with columbite, quartz, and biotite, Sample BP. C, Cassiterite and columbite intergrown with quartz and biotite, Sample RS. D, Columbite attached to biotite. Overgrown zircon on right, Sample RS.

accommodated in fluorite. Hawley and Wobus (1977) reported the modal proportion of K-feldspar component in alkali feldspar phenocrysts, and we used their data and our measurements to calculate the feldspar compositions given in Table IV, along with data from other rocks from the Pikes Peak batholith.

Micas. Most samples of the Redskin Granite contain both biotite and a white mica in small amounts. However, Hawley and Wobus (1977) showed that the relative amounts vary widely and that the average content of white mica is 10% of total micas in the granular facies, 33% of total micas in the porphyritic facies, and 50% of total micas in the fine-grained facies.

Microprobe analyses were made on biotite from samples 3-6, and the results are shown in Table V. Samples 1 and 2 contain only chlorite pseudomorphs after biotite. White micas were analysed in samples 1-4, and the data are also given in Table V. Insufficient white mica in samples 5 and 6 precluded analysis.

The biotite compositions are very similar to each other and to compositions of the three biotites analysed by Hawley and Wobus (1977). They are strongly enriched in Al and F with respect to biotites from other plutons in the Pikes Peak batholith (Barker *et al.*, 1975). They probably also contain significant amounts of Li, because Hawley

and Wobus (1977) reported 0.47 to 0.84 wt% of Li_2O (6 to 10% of the octahedral sites).

The white mica poses a problem in interpretation because, particularly in the fine-grained facies, its texture (fig. 4D) indicates a primary igneous origin, an interpretation which we prefer, yet it is chemically indistinguishable from a 'grey muscovite' typical of the greisen pipes in the Redskin Granite (Hawley, 1969). Li contents of white micas in the granite are unknown. These micas are very Fe-rich dioctahedral micas and perhaps should be called phengites.

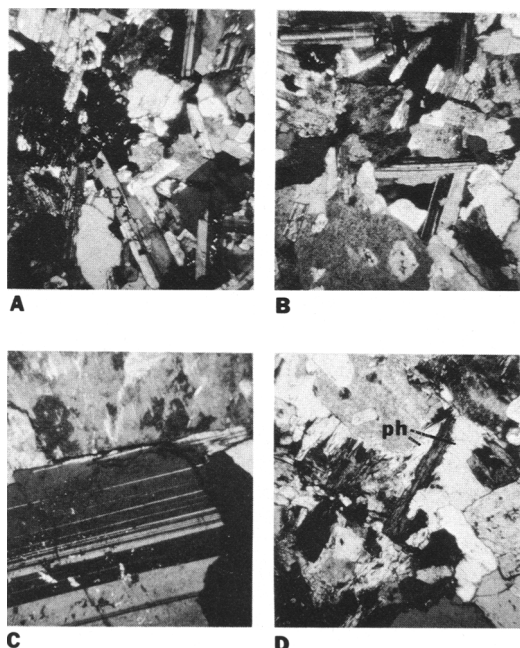


FIG. 4. Primary igneous textures in the Redskin Granite. (All photographs with crossed nicols.) A, Sample 1, plagioclase and alkali feldspar. B, Sample 3, plagioclase and alkali feldspar. C, Sample 5, plagioclase and alkali feldspar. D, Sample 1, phengite (ph) and biotite.

Intensive parameters

Temperature. The normative mineral composition of all facies of the Redskin Granite lies very close to the thermal minimum at $P_{\text{H}_2\text{O}} = 1$ kb in the system $\text{Qz}-\text{Ab}-\text{Or}-\text{H}_2\text{O}$ (Tuttle and Bowen, 1958). This observation led Hawley and Wobus (1977) to conclude that 720 °C and 1 kb were reasonable conditions for the intrusion of the granite. Although they were aware that a problem existed in explaining the composition of the feldspars (they

are very near the end members albite and orthoclase, indicating equilibrium at unusually low temperatures), yet, as shown in photomicrographs (fig. 4A, B, C), there is little textural evidence for subsolidus recrystallization. In fact, application of the compositions in Table IV to the determinative curves of Whitney and Stormer (1977) yields 1 kb crystallization temperatures of 590, 470, and 380 °C for the granular, porphyritic, and fine-grained facies, respectively. These results for phenocryst crystallization temperatures seem very low; however, other evidence suggests anomalously low crystallization temperatures for this granite, as follows:

1. The white micas (Table V) are very Fe-rich and approximate a composition midway between muscovite and Fe-Al celadonite, $\text{KFeAlSi}_4\text{O}_{12}\text{H}_2$. Velde (1965, 1972) did not study this particular composition, but his experiments on similar compositions indicated that this mica, in a F-free system (which the Redskin is not) at 2 kb, would be stable only below 200 °C.

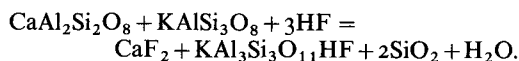
2. The Sn, Nb, and Ta contents of ilmenorutile in the Redskin Granite (Tables I and II) are much lower than the contents of these elements in accessory ilmenorutile found in fresh granites and porphyries at the Henderson molybdenite deposits, Colorado (Desborough and Mihalik, 1980). Columbite is ubiquitous in the Redskin Granite, but is rare at the Henderson deposit. These observations are consistent with lower temperatures of crystallization for the Redskin Granite, in which the Nb and Ti oxides were permitted to develop near-end-member compositions.

3. Although primary magnetite is not abundant, it is present in all Redskin facies. This magnetite is essentially Ti-free, which indicates a very low temperature of crystallization (Buddington and Lindsley, 1964).

4. The concentration of Ti in biotite is 1.8 ± 0.2 wt%, compared with 3.2 ± 0.2 wt% in biotite of the main phase of the Pikes Peak Granite (Barker *et al.*, 1975), which may indicate limited solid solution due to low temperature of crystallization.

5. Megascopic and microscopic features normally associated with low-temperature alteration of granite are conspicuously absent. Chlorite is only weakly developed in some samples and is absent from most. It may be, in part, a product of surface weathering. Feldspars are not significantly sericitized, carbonate minerals are virtually absent, and swarms of liquid-vapour fluid inclusions are rare. All evidence points to essentially closed-system behaviour, with the exception of surficial oxidizing effects due to ground-water, which apparently resulted in the development of hematite after magnetite.

The lowest suggested temperature of equilibration ($< 400\text{ }^{\circ}\text{C}$) seems unreasonable. That portion of the feldspar solvus below $450\text{ }^{\circ}\text{C}$ is poorly known, and small differences in composition are reflected by great differences in temperature. An alternative possibility is that feldspar compositions were controlled by a fluoridation reaction such as:



If the various components in the above reaction are considered to be in the solid or in the liquid state, if this reaction was operative, rigorous application of feldspar thermometry would be invalidated.

The stability of the muscovite-celadonite solid solution is enhanced by F and Li, both of which probably were present in the system in significant amounts.

F (Bailey, 1977) and Rb (Glyuk *et al.*, 1977) are apparently capable of lowering the granite solidus by several hundred degrees. We can only suggest that, in the case of the Redskin Granite, their combined effects, along with other volatile elements, have led to a final crystallization temperature of $500\text{ }^{\circ}\text{C}$ or lower.

Oxygen fugacity. Ilmenorutile and magnetite apparently formed the early stable oxide assemblages in the Redskin. Nothing is known of the $f\text{O}_2$ - T relations of this assemblage. An apparently later assemblage of magnetite-hematite-fluorite suggests that final cooling was along the hematite-magnetite buffer curve. At a water fugacity of 100 bar, an activity of sanidine equal to 0.9, and an activity of magnetite equal to 1.0, an $f\text{O}_2$ - T curve calculated for a typical Redskin biotite, using the equation of Czamanske and Wones (1973) intersects the hematite-magnetite buffer at approximately $420\text{ }^{\circ}\text{C}$. The ferrous-ferric ratios of the biotites analysed by Hawley and Wobus (1977) suggest crystallization at oxygen activities near or below oxygen fugacities defined by the hematite-magnetite buffer (Wones and Eugster, 1965).

Water fugacity. Even though the presence of fluorine may have raised maximum water solubility in the melt to the point at which separation of an aqueous phase occurred very late in the crystallization history (Bailey, 1977), it seems unlikely that water fugacities were much below 1000 bar, the figure suggested by Hawley and Wobus (1977), on the basis of normative composition of the rocks.

Hydrogen fluoride fugacity. Hydrogen fluoride fugacities were extremely high in the Redskin system. $\log f_{\text{H}_2\text{O}}/f_{\text{HF}}$ at $350\text{ }^{\circ}\text{C}$ for all biotites and white micas is 4.1 ± 0.3 (calculated from the equations of Ludington and Munoz, 1975, and Munoz and Ludington, 1977, as amended by Gunow,

1978). Li was ignored in these calculations. The calculated fugacity ratios are about an order of magnitude higher than values for the biotite granite of the Pikes Peak batholith at the same temperature (Ludington, 1974), and are directly comparable to those determined for the Henderson molybdenite deposit by Gunow *et al.* (in press).

Conclusions

The Redskin Granite is a small high-level intrusion protruding from the western edge and probably the top of the Pikes Peak batholith. Compared with the major phase of that batholith, the Redskin has higher concentrations of Rb, Sn, Ta, Nb, and F. The mechanism for this concentration is obscure, but Ludington *et al.* (1979) showed that crystal fractionation could have played only a very small role. They suggested that convection-aided thermogravitational diffusion (Hildreth, 1979; Shaw *et al.*, 1976) was the mechanism responsible for the observed compositional changes in this small cupola at the top of the larger batholith. Probably because of the high fluorine content of the magma the intrusion temperatures were very low, and the pluton cooled relatively slowly as a closed system. Exsolution of a F-rich hydrous fluid did not occur until late in the crystallization history. Thus the rare metals Sn, Nb, and Ta were chiefly trapped in accessory minerals dispersed throughout the rock, apparently precluding formation of economic ore deposits.

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REFERENCES

- Bailey (J. C.), 1977. *Chem. Geol.* **19**, 1-42.
 Barker (F.), Wones (D. R.), Sharp (W. N.), and Desborough (G. A.), 1975. *Precambrian Res.* **2**, 97-160.
 — Hedge (C. E.), Millard (H. T., Jr.), and O'Neill (J. R.), 1976. *Colo. School Mines, Prof. Contr.* **8**, 44-56.
 Buddington (A. F.) and Lindsley (D. H.), 1964. *J. Petrol.* **5**, 310-57.
 Czamanske (G. K.) and Wones (D. R.), 1973. *Ibid.* **14**, 349-80.
 Desborough (G. A.) and Mihalik (P.), 1980. *U.S. Geol. Survey Open-file Rept.* 80-661, 16.
 — and Sharp (W. N.), 1978. *Econ. Geol.* **73**, 1749-51.
 — — Kamilli (R.), Gunow (A.), and Taylor (R. B.), 1978. *9th Reg. Conf. for Study of Min. in Pol. Sec. on Micro-scale, Cent. of Soc. Franc. de Min. et Cristall.*
 Glyuk (D. S.), Bazarova (S. B.), and Trufanova (L. G.), 1977. *Ezhegodnik Sibirsk Inst. Geochim.* (yearbook Siberian Inst. Geochem. for 1976), 170-5.
 Gunow (A. J.), 1978. *Univ. of Colo.* (MS thesis), 287.
 — Ludington (S. D.), and Munoz (J. L.), 1980. *Econ. Geol.* (in press).

- Hawley (C. G.), 1969. *U.S. Geol. Surv. Prof. Paper* **608-A**, 44.
 — and Wobus (R. B.), 1977. *Ibid.* **608-B**, 77.
 — Huffman (C., Jr.), Hamilton (J. C.), and Rader (L. R., Jr.), 1966. *Ibid.* **550-C**, 138-47.
 Hildreth (E. W.), 1979. *Geol. Soc. Amer. Sp. Paper* **180**, 43-75.
 Ludington (S. D.), 1974. Univ. of Colo. (Ph.D. thesis), 167.
 — and Munoz (J. L.), 1975. *Geol. Soc. Am. Abstr.* **7**, 1178.
 — Sharp (W. N.), McKowan (D.), and Barker (F.), 1979. *Ibid.* **11**, 469.
 Munoz (J. L.) and Ludington (S. D.), 1977. *Am. Mineral.* **62**, 304-8.
 Shaw (H. R.), Smith (R. L.), and Hildreth (E. W.), 1976. *Geol. Soc. Am. Abstr.* **8**, 1102.
 Streckeisen (A.), 1976. *Earth Sci. Rev.* **12**, 1-33.
 Tischendorf (G.), 1974. *Int. Geol. Cong. Prog., MAWAM*, **2**, 41-96.
 Turekian (K. K.) and Wedepohl (K. H.), 1961. *Geol. Soc. Am. Bull.* **72**, 175-92.
 Tuttle (O. F.) and Bowen (N. L.), 1958. *Geol. Soc. Am. Mem.* **74**, 153.
 Velde (B.), 1965. *Am. J. Sci.* **263**, 886-913.
 — 1972. *Contrib. Mineral. Petrol.* **37**, 235-47.
 Whitney (J. A.), and Stormer (J. C.), 1977. *Am. Mineral.* **62**, 687-91.
 Wobus (R. A.) and Anderson (R. S.), 1978. *U.S. Geol. Survey J. Res.* **6**, 81-94.
 Wones (D. R.) and Eugster (H. P.), 1965. *Am. Mineral.* **50**, 1228-72.

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