UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Accessory Minerals in the Igneous Host of Molybdenum Ore, Henderson Mine, Colorado

By

George A. Desborough
U. S. Geological Survey
Denver, Colorado, 80225

and

Peter Mihalik
AMAX Extractive Research
and Development, Inc.
Golden, Colorado, 80401

Open-File Report 80-661

1980

This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey standards.

CONTENTS

TABLES

Abstract

Minerals generally considered to be rare accessories of igneous plutonic rocks are minor but ubuquitous in several rock units which occur at the Henderson molybdenum mine, Colorado. The major minerals in fresh Henderson host rocks (dominantly quartz feldspar porphyry and porphyritic granite) are quartz, potassium feldspar, plagioclase, and biotite. The primary magmatic accessory minerals include ilmenorutile, monazite, fluorite, zircon, apatite, magnetite, xenotime, uranium-bearing thorite, aeschynite, columbite, and fluocerite. Ilmenorutile is presnet in all rock units examined except for those which are pervasively altered by hydrothermal solutions. The accessory oxides of interest here occur as discrete euhedral, subhedral, and anhedral grains, polycrystalline aggregates of grains, intergrown minerals, and inclusions. Most ilmenorutile, metamict niobium oxides, and radioactive minerals are chemically inhomogeneous, and uranium, thorium, tantalum, niobium, tin, and scandium are noteworthy rare metals. Yttrium and all of the rare-earth elements are present in wide-ranging amounts in aeschynite, Ilmenorutile is the principal residence of tin.

The chemistry, mineralogy, general distribution, and textural relations of the accessory minerals indicate that they crystallized from the magma. Thus we consider that these accessory minerals preceded the hydrothermal mineralization stages which introduced molybdenite, pyrite, Fe-Mn carbonates, calcite, fluorite, sericite, sphalerite, and galena, which typically occur in quartz veins and veinlets that transect the igneous host.

Introduction

This study was conducted to determine the identity, composition, general distribution, size, and mineralogical association(s) of the magmatic accessory minerals in the igneous host of molybdenum ore at the Henderson mine. This deposit has been extensively drilled and sampled so that samples from widely distributed lateral and vertical locations both within ore zones and adjacent areas were available for study.

A comprehensive report on the geology of the Henderson mine at Red Mountain, Clear Creek County, Colorado, has recently been published by Wallace et al. (1978) and therefore only a brief note on geologic setting is given here. The Henderson molybdenum mine is located about 65 km west of Denver, Colorado, along the Continental Divide and is about about 60 km northwest of the Climax molybdenum mine. The Precambrian Silver Plume Granite hosts a sequence of Tertiary intrusive ore deposits. The sequence, from older to younger, consists of the Tungsten Slide complex, the East Knob porphyry, the Red Mountain porphyry, the Urad porphyry, the Primos porphyry, and the Henderson granite; the distribution of these rock units, in cross section, parallels their age relations with the Red Mountain porphyry at the top, and the Henderson granite at the base (Wallace et al., 1978). The Tungsten Slide complex, near the beginning of the sequence and located high in the composite intrusive system, contains the relatively small Urad molybdenite ore body. The Urad porphyry and the Primos porphyry are the principal hosts of the main molybdenite ore body, but the upper part of the Henderson granite also has a minor amount of molybdenite mineralization. The Urad porphyry and Henderson granite are high-silica, high-alumina, alkalic rocks with very low contents of Ca, Mg, and Fe. Rocks with these bulk chemical characteristics commonly are spatially and/or genetically associated with igneous-related, non-skarn type ore deposits of Mo, Sn, Nb, Ta, and even U. Tischendorf (1974) has recently discussed some of these chemical relations. However, to date, the mineralogical residences of many rare elements have not been delineated sufficiently to determine their economic potential or their possibly utility in geochemical prospecting. This report focuses on the primary accessory minerals in the igneous rocks at the Henderson molybdenite deposit. The occurrence and distribution of these minerals are independent of the later-formed sulfide ore minerals that are extensively discussed by Wallace et al. (1978).

Methods of study

Polished sections, polished thin sections, and polished grain mounts of heavy concentrates were studied microscopically and with the electron microprobe to provide qualitative and quantitative chemical data and to identify minerals. Six polished slabs of rocks showing abundant brown radiation damage in silicates surrounding opaque oxides were studied to determine the identity of the radioactive minerals. Heavy mineral concentrates obtained from hand specimens were studied. Several polished thin sections used in investigations of biotite composition by Alexander Gunow for a thesis study at the University of Colorado also were studied to evaluate the spatial and textural associations of the primary accessory minerals. In addition, two separate samples of mill tailings were processed to extract and study the heavy accessory minerals. These two mill tailings represent aliquots of heavy minerals from several thousand tons of rocks, and thus several hundred grains of heavy minerals were qualitatively identified in these samples. Accessory minerals with simple chemical compositions such as zircon, fluorite, apatite, magnetite, xenotime-YPO_4, and fluocerite-$(Ce,La)F_3$, were not analyzed quantitatively but were studied qualitatively using an energy dispersive detector and multichannel analyzer. Complex minerals such as ilmenorutile-$(Ti,Nb,Fe)_3O_6$, aeschynite-$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$, columbite-$(Fe,Mn)(Nb,Ta)_2O_6$, monazite-$(Ce,La,Nd,Th)PO_4$, and thorite-$(Th,U)SiO_4$ were analyzed quantitatively for selected elements of interest. The quantitative electron microprobe data obtained are shown in tables that follow.

Accessory minerals of interest

Magnetite.--Magnetite is a primary accessory in all rock units, and also is a common hydrothermal mineral. It contains less than about 0.1 weight percent of titanium, and other elements are not detectable. Morphologically it is generally euhedral to subhedral and mineral inclusions are not microscopically conspicuous.

Ilmenorutile.--This mineral is a major primary magmatic accessory oxide in all igneous host rocks. In addition to titanium, variable amounts of niobium, tantalum, iron, and tin are present. Where it was hydrothermally altered, pure rutile developed. All ilmenorutile occurs as discrete anhedral grains that are commonly near cogenetic minerals such as aeschynite, magnetite, monazite, zircon, biotite, or other less abundant accessory minerals. It is generally, but not invariably, opaque in polished thin sections. Moderate reflectance, good polish, and strong anisotropy distinguish it from the other accessories in reflected light microscopy studies. Chemically, the mineral varies widely in composition and both intragrain and intergrain chemical inhomogeneity are typical. Although titanium, niobium, iron, tantalum, and tin are the principal major and minor elements, thorium, scandium, uranium, manganese, and yttrium can be present in concentrations of 0.1 or more weight percent.

A sample of heavy mineral table concentrate, taken in 1977, was leached with HCl and HF. This residue was then examined in reflected light and grains were quantitatively analyzed for Ta, Sc, and U with the electron microprobe. The results, for inclusion-free areas, on 45 ilmenorutile grains are as follows, in weight percent:

	Ta_2O_5	Sc_2O_3	UO_2
Mean	1.2	0.15 in 9	0.1 in 14 grains;
Std. dev.	0.9	grains; <0.1	0.2 in 1 grain;
Range	<0.1-4.4	in 36 grains	<0.1 in 30 grains.

These data show a high degree of inhomogeneity of Ta, Sc, and U among the ilmenorutile grains; comparable results were obtained by Desborough and Sharp (1978a) for ilmenorutile concentrates from the Climax molybdenum mine, Colorado.

All of the analytical data for ilmenorutile show a very high degree of chemical inhomogeneity for all elements in samples from small volumes of rock, as well as samples from very large volumes of rock. Quantitative microprobe analyses of 15 grains of ilmenorutile in a polished grain mount of heavy minerals extracted from a crushed hand specimen gave the following, in weight percent:

	TiO_2	Nb_2O_5	FeO	Ta_2O_5	UO_2	ThO_2	Y_2O_3
Mean	81.5	12.1	6.1	1.1	0.1	0.1	<0.1 in 11 grains;
Std. dev.	14.9	10.0	5.5	1.4	0.2	0.1	0.1 in 3 grains;
Range	49.2-97.3	1.7-35.3	1.0-17.5	<0.1-4.9	<0.1-0.7	<0.1-0.3	0.4 in 1 grain

In addition, quantitative microprobe analyses for 12 ilmenorutile grains in heavy concentrates obtained from six hand specimens gave the following, in weight percent:

	TiO_2	Nb_2O_5	FeO	Ta_2O_5	UO_2	ThO_2
Mean	77.5	15.9	5.9	1.4	0.3 for 1 grain;	0.2 for 1 grain
Std. dev.	18.6	12.9	5.3	1.6	0.1 for 2 grains	
Range	46.4-97.4	2.4-39.8	0.1-15.4	<0.1-5.1		

A mill circuit sample obtained during 1978 production was studied to determine the concentration of tin, tantalum, and niobium in ilmenorutile. Data for 69 inclusion-free grains are reported in table 1. The analytical data for these grains are given in four groups of less than 20 grains each due to computational limitations of on-line microprobe analysis. These data show that ilmenorutile contains a significant concentration of tin, as well as niobium and tantalum. Tin is present in all grains, ranging from 0.1 to 3.6 percent SnO_2. These data demonstrate the substantial intergrain inhomogeneity, and relatively wide range in concentrations of tin, tantalum, and niobium.

For comparison with other ilmenorutile data, a study of the tungsten-bismuth-molybdenum deposit at Mount Pleasant, New Brunswick, by Petruk (1973, table 3, p. 120) showed compositional data for 14 rutile grains which averaged (weight percent) 1.2 SnO_2, 3.5 Nb_2O_5, and 0.3 Ta_2O_5.

Some grains of opaque accessory minerals are bordered by a brown zone in the normally white surrounding silicates. These brown halos seem to be the result of radiation damage. The opaque grains studied consist of ilmenorutile and a metamict niobium oxide whose X-ray diffraction pattern (after heating) and chemical composition compare well with aeschynite. Ilmenorutile forms a border phase adjacent to the aeschynite.

Table 1.--Concentration of tin, tantalum, and niobium in ilmenorutile from a mill circuit concentrate, determined by electron microprobe analysis.

[Number of grains in each group as follows: 1,19; 2,17; 3,17; and 4,16. Data in weight percent.]

	SnO_2	Ta_2O_5	Nb_2O_5
		Group 1	
Mean	0.9	1.0	15.8
Std. dev.	0.6	0.8	7.3
Range	0.2-3.6	<-3.4	0.7-30.2
		Group 2	
Mean	0.7	0.9	12.5
Std. dev.	0.5	1.0	5.6
Range	0.2-1.7	0.1-3.6	4.5-23.4
		Group 3	
Mean	0.8	0.9	12.3
Std. dev.	0.4	0.6	5.8
Range	0.3-1.9	0.1-3.8	4.2-23.0
		Group 4	
Mean	0.9	1.4	16.1
Std. dev.	0.5	1.2	8.1
Range	0.1-1.7	0.2-4.1	3.6-37.0

Both minerals were analyzed for the 24 elements listed in table 2. In addition, zirconium, fluorine, and holmium were sought, but were not detected. The ilmenorutile in this two-phase association contains more niobium and tantalum than the mean values reported in table 1, but the values still are within the reported range. It is considered that the ilmenorutile and aeschynite in this association developed by subsolidus unmixing of a complex titanium-niobium oxide which was the stable phase at a higher temperature.

Aeschynite.--Aeschynite occurs in association with ilmenorutile, as mentioned above, where the radioactive grains were large enough to produce megascopically visible brown radiation damage halos in adjacent silicates. It has also been found as 10-25 μm inclusions in a few grains of ilmenorutile. However, in one polished thin section of unmineralized Henderson granite, four grains of aeschynite were identified by optical methods combined with electron microprobe analysis. All four grains are anhedral, are slightly translucent, and are dark red brown in transmitted light. The largest grain, 400 μm diameter, is adjacent to much smaller grains of monazite, fluocerite, and ilmenorutile. Another grain, about 120 μm in diameter, is adjacent to magnetite and biotite. A third grain, 80 μm in diameter, occurs adjacent to monazite. A fourth grain, 60 μm in diameter is adjacent to, but not enclosed by, a much larger ilmenorutile grain. The spatial association of aeschynite with the other accessory minerals probably indicates that it formed by late magmatic crystallization. The quantitative chemical data for four aeschynite grains bordered by ilmenorutile show (table 2) that it is an important carrier of certain rare metals including niobium, tantalum, uranium, thorium, tin, and some of the heavy rare earths.

Table 2.—Composition of ilmenorutile and adjacent aeschynite for four mineral pairs.

[Weight percent, determined by electron microprobe analysis. < indicates element was not detectable. Results represent the mean of four areas. ILR = ilmenorutile, AES = aeschynite.]

Specimen No.	PM607A1		PM607A2		PM607H4		PM655X	
	ILR	AES	ILR	AES	ILR	AES	ILR	AES
TiO_2	57.0	17.6	53.7	17.1	51.8	17.9	53.6	4.9
Nb_2O_5	25.0	30.5	26.6	32.0	25.6	30.9	25.1	39.3
FeO	12.8	1.8	13.1	2.2	13.2	1.5	12.9	13.8
Ta_2O_5	3.4	3.2	4.7	3.7	4.4	3.6	5.3	3.7
SnO_2	0.5	0.3	0.7	0.2	0.4	0.3	1.2	1.0
ThO_2	0.2	13.2	0.2	12.8	0.4	15.8	0.2	5.1
UO_2	<	4.6	0.1	2.8	0.1	4.9	0.1	12.2
Sc_2O_3	0.3	<	0.3	<	0.3	0.1	0.2	1.1
MnO	<	0.1	<	0.1	<	0.1	0.2	2.6
Y_2O_3	<	3.6	<	4.4	<	3.2	<	4.9
CaO	<	3.0	<	4.4	<	3.9	<	0.5
La_2O_3	<	3.2	<	1.7	<	3.9	<	<
Ce_2O_3	<	8.8	<	6.3	<	6.8	<	0.6
Pr_6O_{11}	<	1.5	<	1.2	<	1.2	<	0.2
Nd_2O_3	<	4.6	<	4.9	<	3.1	<	1.5
Sm_2O_3	<	1.3	<	1.6	<	1.2	<	0.9
Eu_2O_3	<	0.1	<	<	<	<	<	<
Gd_2O_3	<	1.6	<	1.6	<	1.5	<	1.1
Tb_2O_3	<	0.1	<	0.1	<	0.2	<	0.3
Dy_2O_3	<	1.0	<	1.2	<	1.0	<	1.8
Er_2O_3	<	0.4	<	0.4	<	0.5	<	1.5
Tm_2O_3	<	<	<	0.1	<	<	<	0.4
YbO_2	<	0.5	<	0.3	<	0.2	<	2.1
Lu_2O_3	<	<	<	<	<	<	<	1.5
Total	99.2	101.0	99.4	99.1	96.2	101.9	98.9	101.0

Columbite.--Columbite is apparently the least abundant niobium-bearing mineral in the Henderson igneous suite. It occurs as small inclusions in ilmenorutile, as separate grains adjacent to ilmenorutile, and in a few discrete grains found in heavy concentrates obtained from hand specimens and mill tailings. Chemical data for certain major and minor elements in three columbite grains, given in table 3, show that minor, but perhaps significant amounts of uranium, thorium, tin, scandium, yttrium, and dysprosium are present. Columbite previously has been recognized in ilmenorutile concentrates from the Climax molybdenum mine where it occurs as small inclusions in ilmenorutile (Desborough and Sharp, 1978a).

Monazite.--Monazite is a relatively abundant accessory mineral in the Henderson igneous suite, and most frequently forms small to large (10-500 μm) anhedral grains near other accessory minerals. Monazite is known to host minor amounts of uranium which is of special interest here. Electron microprobe analysis gave a mean of 0.15, standard deviation of 0.05, and a range of 0.1-0.20 weight percent UO_2 for 42 grains. The mean is comparable to quantitative fluorometric data of 0.12 weight percent UO_2 for a monazite concentrate from the Climax molybdenum mine which was analyzed by Frederick Ward (U.S. Geological Survey, 1978, oral commun.).

The thorium content of the monazites in the heavy concentrates ranges from 1.2 to 2.6 weight percent ThO_2.

Table 3.--Quantitative electron microprobe analysis for certain elements in columbite from three specimens.

[Weight percent, n.a. = not analyzed, < = below detection limit.]

Specimen No.	PM651	PM810	PM816
Nb_2O_5	61.9	70.5	64.8
TiO_2	7.6	7.4	17.6
FeO	12.2	16.9	6.6
MnO	7.5	1.0	<0.1
Ta_2O_5	2.5	3.8	3.8
Sc_2O_3	3.0	n.a.	n.a.
SnO_2	0.8	n.a.	n.a.
Dy_2O_3	1.7	n.a.	n.a.
UO_2	0.1	<0.1	2.4
ThO_2	0.1	<0.1	1.0
Y_2O_3	<0.1	<0.1	0.8
Total	97.4	99.6	97.0

Thorite.--Thorite occurs as either anhedral or euhedral grains, and is generally found in proximity to other accessories. It also occurs as small (<50 μm) grains in the major silicate minerals. The occurrence of euhedral thorite in separate chemically inhomogeneous zoned grains may indicate crystallization early during cooling of the magma before the other non-silicate accessory minerals crystallized. Quantitative electron microprobe analysis of 47 grains gives an average of 5.0 weight percent of UO_2, a standard deviation of 2.5, and a range of 2.3-7.8. Thus thorite carries uranium, but usually the grain size is so small that recovery of significant amounts of uranium from thorite obtained from heavy mineral concentrates alone is unlikely.

Rare heavy minerals.--Only a few grains of wolframite, cassiterite, brannerite, and uraninite were found in heavy concentrates from the mill circuit samples. None of these minerals were found in polished rock slabs, or in concentrates from hand specimens. Therefore it is thought that these minerals largely formed during hydrothermal mineralization, or by thermal redistribution of components in earlier accessory minerals during mineralization.

Rare element distribution in accessory minerals

Niobium, tantalum, tin, and scandium occur principally in ilmenorutile and aeschynite in the Henderson igneous suite. Significant amounts of uranium, thorium, and rare earths are also found in aeschynite. Monazite and fluocerite are major hosts for the light rare earths, and monazite contains minor thorium and about 0.1 weight percent of uranium. Thorite is the only mineral in which thorium is a major constituent and it also contains a few percent of uranium. The presence of these rare elements in variable concentrations in several different coexisting accessory minerals reflects complex element partitioning during accessory mineral crystallization. In addition, this distribution in several different heavy minerals may inhibit recovery of the rare elements as by-products, or at least constrains the variety of extraction methods that might be used.

A significant result of the present study is the recognition of ilmenorutile and aeschynite as important accessory minerals in the igneous host rocks of molybdenum ore. The presence of aeschynite in "unmineralized" Henderson granite is important because this mineral has not normally been considered a rock-forming accessory mineral. Ilmenorutile is particularly important because it carries such a variety of rare elements. Tin, in particular, occurs within ilmenorutile, which ranges from 0.1 to 3.6 weight percent SnO_2 in all grains studied. The 10 to 70 parts per million of tin found in "unmineralized" igneous rocks at the Henderson deposit probably is contained largely in ilmenorutile, although aeschynite may account for a minor part. In further support, of the several thousand grains in heavy concentrates studied, no more than 5 cassiterite grains were found.

A recent study of the Precambrian Redskin Granite, which averages 16 parts per million of tin, shows that ilmenorutile probably hosts most of the tin in this highly silicic alkali-granite (Desborough and Sharp, 1978b), even though the content of SnO_2 in ilmenorutile is only 0.1 to 0.6 weight percent.

Acknowledgments

We are grateful to Dr. Robert J. Kamilli, Geology Department, Henderson Mine, Climax Molybdenum Company, for his generous cooperation in providing samples and consultation. We also thank Mr. Alexander Gunow, Geology Department, University of Colorado, for providing samples and consultation concerning the Henderson deposit, and Ms. Anita Gorski of AMAX Extractive Research and Development, Inc. for preparation of the mineral separates and polished sections.

REFERENCES

Desborough, G. A., and Sharp, W. N., 1978a, Tantalum, uranium, and scandium in heavy accessory oxides, Climax molybdenum mine: ECON. GEOL., v. 73, p. 1749-1751.

______1978b, Niobium, tantalum, and tin in opaque oxides of the Redskin Granite, Colorado: Mineral. Soc. Bull. No. 41, p. 2.

Petruk, W., 1973, The tungsten-bismuth-molybdenum deposit of Brunswick Tin Mines Limited—Its mode of occurrence, mineralogy and amenability to mineral beneficiation: Canad. Inst. Mining and Metal. Bull., v. 66, no. 732, p. 113-130.

Tischendorf, G., 1974, Geochemical and petrographic characteristics of silicic magmatic rocks associated with rare-element mineralization: Int. Geol. Cong. Prog., MAWAM, v. 2, p. 41-96.

Wallace, R. W., MacKenzie, W. B., Blair, R. G., and Muncaster, N. K., 1978, Geology of the Urad and Henderson molybdenite deposits, Clear Creek County, Colorado, with a section on a comparison of these deposits with those at Climax, Colorado: ECON. GEOL., v. 73, p. 325-368.