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SULFUR ISOTOPE INVESTIGATION OF THE GOLD-QUARTZ DEPOSITS OF THE YELLOWKNIFE DISTRICT[1]

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CONTENTS

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ABSTRACT

Sulfides in the orebodies and their associated alteration haloes, the metamorphic facies of the greenstone belt, and the neighboring granodiorite have been examined in detail. Most of the samples investigated are slightly enriched in S^{34} with respect to the meteoritic standard. Although the overall range is small (about 1.5%), significant variations were found between sulfides in the granodiorite and in the metamorphic facies of the greenstone belt. A direct correlation exists between the isotopic ratio and the distance from the granodiorite-greenstone contact; sulfides in the granodiorite are the most enriched in S^{34} whereas sulfides in the metamorphic facies contain progressively less S^{34} outward from the granodiorite contact.

Sulfides in early tension fractures are consistently lighter (i.e. they contain more S^{32}) than the sulfides in the surrounding greenstones, whereas sulfides in the later gold-quartz lenses are heavier than those in the associated alteration zones. In addition, profiles across the country rock, alteration zones, and gold-quartz lenses indicate that the heavy isotope has been preferentially retained in the alteration zones with the maximum enrichment in the ore. However, in the late cross-cutting quartz-carbonate lenses the lighter sulfur isotope has been preferentially concentrated.

The isotopic studies indicate that the primary sulfur isotopic distribution of the district was modified by granitization and metamorphism during which the S^{32} was mobilized to a greater extent, leaving the sulfides in the regions with the higher thermal histories enriched in S^{34}. The subsequent formation of the gold-quartz lenses was associated with intense chemical activity and the S^{32} was again more mobile, resulting in an enrichment of S^{34} in the alteration zones and in the ore.

INTRODUCTION

For several years the Geological Survey of Canada has carried out a detailed geological and geochemical investigation of the gold-quartz deposits of the Yellowknife District, Northwest Territories, the results of which may be found in publications noted in the references. Recently, facilities for isotope research have been developed in the Survey laboratories in Ottawa, and a sulfur isotope investigation of the region undertaken.

One interpretation of the geochemical data obtained, suggests that the ore constituents of the gold-quartz orebodies were derived from the associated country rocks by diffusion. If this is the case, and the process of metamorphic secretion was responsible for the formation of the orebodies, the possibility exists that the isotopes of sulfur may have been fractionated, and the observed isotopic ratios may be indicative of the mechanism responsible for the concentration of the ore. This investigation has revealed that although the overall isotopic variation is small, significant trends are distinguishable. The majority of the specimens examined contain sulfur enriched in the heavier isotope (i.e. S^{34}) compared with the meteoritic troilite sample employed as a standard.

The sulfur isotope distribution has been correlated with the geology and geochemistry of the district and evidence is presented to support the hypothesis that the lighter sulfur isotope (i.e. S^{32}) has been mobilized more readily and that the residual sulfur has been consequently enriched in the heavier isotope. The observed enrichment is attributed to two distinct processes believed to be subsequent in time. These are: 1) a thermal gradient produced during early granitization and regional metamorphism, and 2) chemical and pressure gradients developed during the subsequent formation of the large shear zones containing the gold-quartz orebodies.

GEOLOGICAL SETTING OF THE DEPOSITS

The general geology of the Yellowknife district was described first by Stockwell and Kidd (22) and later, in more detail, by Jolliffe (14, 15). More recently a description of the geology and a structural analysis of the principal ore-bearing shear zones of the greenstone belt was published by Henderson and Brown (13). The geology of the orebodies of the Con-Rycon and Giant Mines was described by Campbell (8), Dadson and Bateman (12), Dadson (11), Bateman (2), Brown and Dadson (6), Boyle (5), and Brown, Dadson and Wrigglesworth (7). The mineralogy of the orebodies has been described by Ridland (20) and Coleman (9, 10). These authors have covered the geology and mineralogy of the district and gold deposits in considerable detail, and the brief description that follows gives a summary of the most important features and provides a background for discussing the isotope geology of sulfur within the district.

The consolidated rocks within the district are Precambrian in age (4, Fig. 1, p. 1508). The oldest rocks are greenstones consisting of a succession of massive and pillowed andesite and basalt flows with interbedded dacite flows, graphitic and siliceous tuffs, and agglomerates (Division A, Yellowknife Group). These rocks contain numerous gabbro and diorite sills and are cut by dikes of similar composition. Quartz-feldspar porphyry dikes and masses cut the greenstones throughout the district, but are found in greatest profusion in the northern part of the belt, particularly in the area east and southeast of Ryan Lake. The greenstones are overlain by a thick series of greywacke, argillite, slate, quartzite, and their metamorphic equivalents (Division B, Yellowknife Group).

Three large granitic masses occur within the district. One flanks the greenstone belt on the west, and another forms a large mass south of the sedimentary area. The third granitic mass, known as the Prosperous Lake granite, occurs east of Prosperous Lake. Field and chemical evidence suggest that the western granitic mass originated by granitization of a great series of sedimentary rocks that once lay stratigraphically below the greenstones. The Prosperous Lake granite and southeastern granitic mass were probably derived by granitization of parts of the Yellowknife sediments.

The greenstones have been extensively altered by regional metamorphism. The metamorphic facies (4, Fig. 2, p. 1509) are distinctly related to the granodiorite-greenstone contact and comprise a contact amphibolite facies, an intermediate epidote amphibolite facies, and a poorly developed greenschist facies

Two metamorphic facies are clearly defined in the Yellowknife sediments and are related to the Prosperous Lake and southeastern granitic masses (4). Next to these granitic masses a zone of nodular quartz-mica schist and hornfels containing garnet, andalusite, staurolite, and cordierite is present. This facies grades sharply into relatively unaltered greywacke, argillite, arkose, and slate.

Pegmatites, containing quartz, feldspar, mica, and locally typical pegmatite minerals such as tourmaline, beryl, and spodumene, are abundant in the Prosperous Lake granite and the quartz-mica schist and hornfels facies of the Yellowknife sediments.

Diabase dikes and basic sills are the youngest consolidated rocks in the district. These have a gabbroic to ultra-basic composition and are relatively unaltered except where cut by late faults.

The greenstone rocks of the district are folded into a broad northeasterly-plunging asymmetrical syncline. The northwest limb (greenstone belt) consists of a simple homoclinal succession of volcanic flows that dip and face southeast. The southeast limb is overturned and is in part folded into a subsidiary anticline. The sediments of the Yellowknife group are complexly folded into tight isoclinal folds, which in turn have been cross-folded.

Two ages of shear zones occur in the greenstone belt (4): (a) early shear zones that parallel the lava flows in strike and dip and contain a few small high grade gold-quartz lenses, e.g. Ranney system; and, (b) shear zones that transect the lava flows and contain the large economic gold-quartz veins and lenses of the district, e.g. Con system. The Giant-Campbell shear zone system is the major ore-bearing system in the district and probably formed along a major thrust fault zone. The smaller but productive Con and Negus-Rycon systems are subsidiaries of this large system.

In the shear zone systems the principal ore controls are shear zone junctions and flexures and drag-folded parts of the large schist zones. The deposits are veins, lenses, and complex bodies of quartz enveloped by distinctive alteration haloes (Fig. 1).

In the sediments of the Yellowknife group, gold-quartz veins and lenses are developed in small faults, drag folds, saddle reefs, ruptured and sheared axes of isoclinal folds, and other structures, all formed during the complex folding of the sedimentary rocks. Structurally these veins and lenses are isolated bodies, unconnected to any system of fractures or faults along which hydrothermal solutions could have travelled.

Some of the gold-quartz lenses in the greenstones cut the last phase of granite dikes; therefore, it can be assumed that the deposits were formed after the emplacement and consolidation of the granitic mass flanking the greenstone belt. The lenses also cut the quartz-feldspar porphyry dikes and masses, thus ruling out the possibility that these bodies were the source of hydrothermal solutions from which the lenses were derived. In the sedimentary area the quartz lenses and veins appear to be contemporaneous with

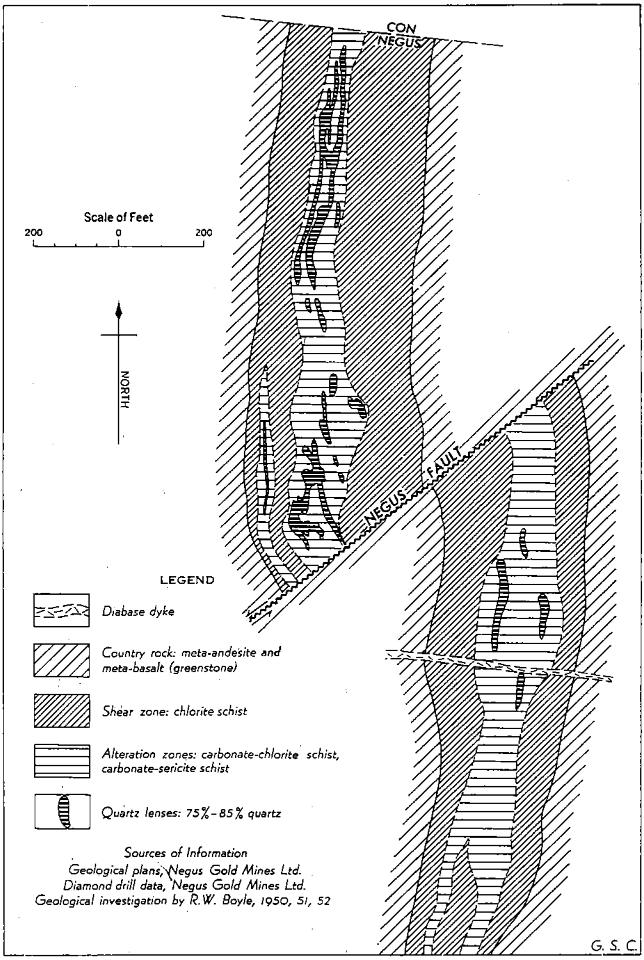

FIG. 1. Plan of geology, 1,775-foot level, Negus Mine, Campbell System.

the metamorphism of the sediments and the formation of the Prosperous Lake granite.

Post-diabase faults and fractures cut all rocks in the district. In these faults quartz-hematite lenses and "giant quartz veins" are localized at or near junctions and flexures.

MINERALIZATION OF THE DISTRICT

The age relationships of the various quartz, carbonate, and sulfide deposits are listed below, the oldest first. Pertinent features of each type of deposit are included.

Greenstone Belt

1. Formation of quartz lenses in tension fractures in massive flows and dikes. These lenses contain essentially quartz with minor amounts of pyrite. They exhibit no marked alteration zones, but chemical analyses on traverses across the rocks adjacent to the lenses suggest a transfer of silica from the walls into the tension fractures (5).

2. Formation of quartz lenses and veins in (a) parallel shear zone systems; (b) transecting shear zone systems. The age relationships of these two types of quartz lenses are uncertain. Presumably they are contemporaneous. The principal minerals in the lenses are quartz, carbonates, sericite, pyrite, arsenopyrite, chalcopyrite, sphalerite, pyrrhotite, scheelite, stibnite, various sulfosalts, galena, gold, and aurostibite. The paragenetic sequence of the sulfides is pyrite, arsenopyrite, pyrrhotite, chalcopyrite, and sphalerite, all more or less contemporaneous, followed by stibnite, sulfosalts, galena, locally sphalerite, gold, and aurostibite. The quartz lenses are generally enveloped by a carbonate-sericite-pyrite-arsenopyrite alteration halo that grades imperceptibly into the chlorite-carbonate or chlorite schist of the shear zones (Fig. 1). Chemical analyses of the alteration zones indicate that carbon dioxide, water, sulfur, and potassium were added to the highly altered zones, and that some silica, calcium, sodium, iron, magnesium, and manganese were removed. Boyle (3, 4, 5) has presented data suggesting that the carbon dioxide, water, and sulfur were derived from the country rocks and that they were drawn into the shear zones as a result of the pressure gradients resulting from dilatancy. In the shear zones these volatile compounds reacted with various silicates to form carbonates, sericite, chlorite, and sulfides. During these reactions silica was released in large quantities and migrated into, and was precipitated in local dilatant zones within the shear zones.

3. Formation of quartz-carbonate stringers and lenses that cross-cut the early gold-quartz lenses. These bodies contain essentially quartz, carbonates, chalcopyrite, tetrahedrite, galena, arsenopyrite, and minor amounts of sulfosalts; alteration haloes are absent. The quartz-carbonate stringers and lenses are isolated bodies and appear to represent fillings of tension fractures. The available facts suggest that their constituent elements were derived locally from the shear zones and early gold-quartz lenses.

4. Formation of late faults and fractures followed by deposition of quartz lenses and "giant quartz veins." These bodies contain essentially quartz and hematite with small quantities of pyrite and chalcopyrite. The principal alteration effects in the rocks adjacent to the quartz bodies are a mild silicification, sericitization, and chloritization.

5. Precipitation of carbonates and pyrite from underground waters carrying various sulfates, chlorides, and carbonates. This late mineralization is presently active.

Sedimentary Area

1. Formation of pegmatites containing essentially feldspar, quartz, muscovite, tourmaline, and locally beryl, spodumene, and tantalite-columbite.

Sulfides are rare or absent. The age of the pegmatites with respect to the quartz bodies described below is uncertain. Some pegmatites are cut by these quartz bodies; others cut across the gold-quartz lenses.

2. Formation of quartz lenses and irregular bodies in faults, drag folds, ruptured and sheared axes of isoclinal folds, and other structures. These contain essentially quartz with small amounts of pyrite, sphalerite, galena, pyrrhotite, arsenopyrite, scheelite, and gold. Two or more generations of quartz may occur in the lenses. The sulfides are generally later than the quartz, but there is relatively little age difference between the various sulfides. Most of the quartz bodies have no well-developed alteration zones, but a few are marked by a narrow zone of tourmalinized and sericitized rock.

3. Formation of late faults and fractures followed by deposition of quartz lenses and "giant quartz veins." These are the same age as those in the greenstone belt and are identical in most respects.

SULFUR ISOTOPE VARIATIONS IN NATURE

The pioneer work of Thode, Macnamara, and Collins (23), Macnamara and Thode (16), Macnamara, Fleming, Szabo, and Thode (17), Thode, Macnamara, and Fleming (24) and Thode, Wanless, and Wallouch (25) has shown that considerable variation exists in the sulfur isotope distribution in nature. Tudge and Thode (26) and Sakai (21) have determined the partition function ratios of some isotopic molecules of sulfur and have calculated the fractionation factors for certain exchange reactions at various temperatures. The overall isotopic variation between $SO_4^= \rightleftarrows H_2S$ is calculated to be 7.4 percent at 25° C, decreasing to about 1 percent at 500° C. Generally speaking, one finds a variation of this order of magnitude in nature with the heavier sulfur isotope, sulfur-34, concentrated in sulfate minerals and in sea water whereas the lighter isotope, sulfur-32, is enriched in sedimentary sulfides. Analyses of meteoritic troilite (16) have failed to reveal any variations within the precision of the results and, consequently, the determined S^{32}/S^{34} ratio of 22.22 has been adopted as the standard for all sulfur isotope studies.

The range of the isotopic results reported by Thode (23), Ault, and Kulp (1), and others is illustrated in Figure 2. The meteoritic standard has been assigned a value of zero and results plotted below the zero line have positive values indicating that they contain more S^{34} than the meteoritic standard, while results appearing above the zero line are enriched in S^{32}. It will be noted that sea water sulfate has a very uniform isotopic ratio (1) indicated by the dashed line.

The Yellowknife results reported in this paper fall within a narrow range close to the meteoritic value. The total range of the isotopic distribution for 140 sulfide samples from the region is only 1.5 percent with the average value falling slightly below meteoritic, at + 2.2‰. The majority of the results fall within the narrow limits + 0.5 to + 4.0‰ indicated by the solid bar. Only six samples have ratios lighter than meteoritic, and two others have an isotopic composition identical with the standard. Prior to the development of mass spectrometric apparatus employing specialized methods of sample introduction and simultaneous ion beam collection (18, 27), it would have been impossible to distinguish between results falling within such narrow limits, and one would have been forced to the conclusion that the isotopic distribution was constant throughout the district.

In addition to the sulfides, four sulfate samples separated from the mine waters were analyzed. The sulfate sulfur values, ranging from + 9 to + 26‰, are all considerably heavier than the sulfides.

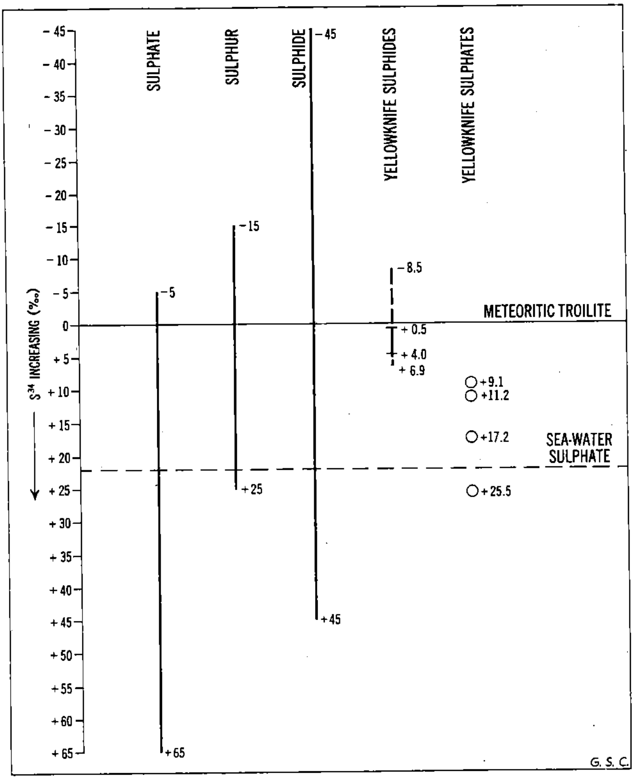

FIG. 2. Sulfur isotope distribution in nature.

SULFUR ISOTOPE DISTRIBUTION IN COUNTRY ROCKS OF GREENSTONE BELT

The sulfur isotope values are presented in accordance with the time sequence of geologic events as outlined under the general geology and mineralization of the district. The significance and interpretation of the observed trends will, in general, be reserved for the concluding sections.

Granitic Rocks (Granodiorite and Quartz-feldspar Porphyry)

The sulfur isotope ratios determined for the granitic rocks west of Yellowknife Bay are given in Table 1. The value for the western granodi-

TABLE I

GRANITIC ROCKS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
91	Py from granodiorite*	Western granodiorite.	+5.0
356	Py from fresh porphyry. Exposed dike.*	300' level Negus mine.	+6.8
400	Py from porphyry. Exposed dike.*	Negus mine.	+3.1
392	Py from porphyry. Exposed dike.*	Rycon mine.	+2.9
65	Py from quartz-feldspar porphyry. All bodies.*	Rycon, Con, and Negus mine areas.	+3.1
		Average of porphyry	+4.0

*Represents composite chip sample in all tables.

Symbols in all tables. Py, pyrite; pyrr, pyrrhotite; asp, arsenopyrite; sulfs, sulfosalts; sp, sphalerite; cp, chalcopyrite; td, tetradhedrite; sb, stibnite; gn, galena.

TABLE 2

GREENSTONE BELT ROCKS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
87	Py from amphibolite facies. All traverses across facies.*	Greenstone belt.	+1.9
86	Py from epidote amphibolite facies. All traverses across facies.*	Greenstone belt.	+1.1
84	Py from epidote amphibolite facies, across 1500'.*	Southeast of Stock Lake	+1.6
118	Py from epidote amphibolite facies, across 50'.*	Negus-Rycon system adjacent to Negus mine.	+1.1
123	Py from epidote amphibolite facies, across 250'.*	Campbell system. Adjacent to Negus mine.	+0.6
362	Py from epidote amphibolite facies (Slightly chloritized), across 100'.*	Giant system. Adjacent to 425' level, Giant mine.	+1.6
357	Py from epidote amphibolite facies, across 20'.*	Giant system adjacent to Giant mine	+1.3
104	Py from epidote amphibolite facies, across 100'.*	Giant system, adjacent to Akaitcho mine.	+2.2
	Average of epidote amphibolite facies (7 samples)		+1.4

TABLE 3

TUFFS

A) GRAPHITIC

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
37	Massive py associated with large amounts of graphite[1].	Ranney tuff, west of Giant mine.	+5.0
38	Massive pyrr associated with No. 37[1].	Ranney tuff, west of Giant mine.	+2.0
27	Py associated with pyrr in graphitic bed[1].	Giant mine.	+2.7
33	Pyrr associated with No. 27[1].	Giant mine	+2.4
101	Py in graphitic tuff[1].	Akaitcho mine area.	+3.3
345	Py in graphitic banded tuff[1].	Lynx area 1/2 mile north of No. 101.	+5.6
		Average	+3.5

B) SILICEOUS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
116	Py in cherty bands in tuff. <u>No</u> graphite.	A.E.S. tuff, west of Akaitcho area	-0.9
349	Py in chloritized tuff.	A.E.S. tuff, west of Akaitcho area.	-0.3
35	Py with pyrr and magnetite[2].	Ranney tuff, David Lake.	-2.7
36	Pyrr with magnetite[2].	Ranney tuff, David Lake.	-0.9
		Average	-1.2

[1] Average carbon content 1.28%
Average sulphur content 1.45%

[2] Average carbon content 0.10%
Average sulphur content 0.1 to 0.5%

orite (No. 91) was obtained from a composite sample composed of fresh chips collected west of the granodiorite-greenstone contact over a distance of some fifteen miles and, therefore, represents an average isotope distribution for a very large volume of rock. The isotopic result, + 5‰, indicates that the granodiorite contains more S^{34} than the meteoritic standard. The quartz-feldspar porphyries also contain sulfur enriched in S^{34}, and in one instance (No. 356) the sulfides of a porphyry contain more S^{34} than found in the sulfides of the western granodiorite.

Greenstones

Proceeding east from the granodiorite-greenstone contact composite samples of fresh rock were taken on traverses across the amphibolite and epidote amphibolite facies throughout the length of the greenstone belt. From the sulfur isotope ratios given in Table 2, it is apparent that sulfide minerals of the greenstone rocks contain much less S^{34} than those found in the western granodiorite and quartz-feldspar porphyries. Furthermore, it will be noted that the value for the amphibolite facies (No. 87) is + 1.9‰ which is heavier than the average of + 1.4‰ determined for seven samples collected from the epidote amphibolite facies. With the exception of the single sample

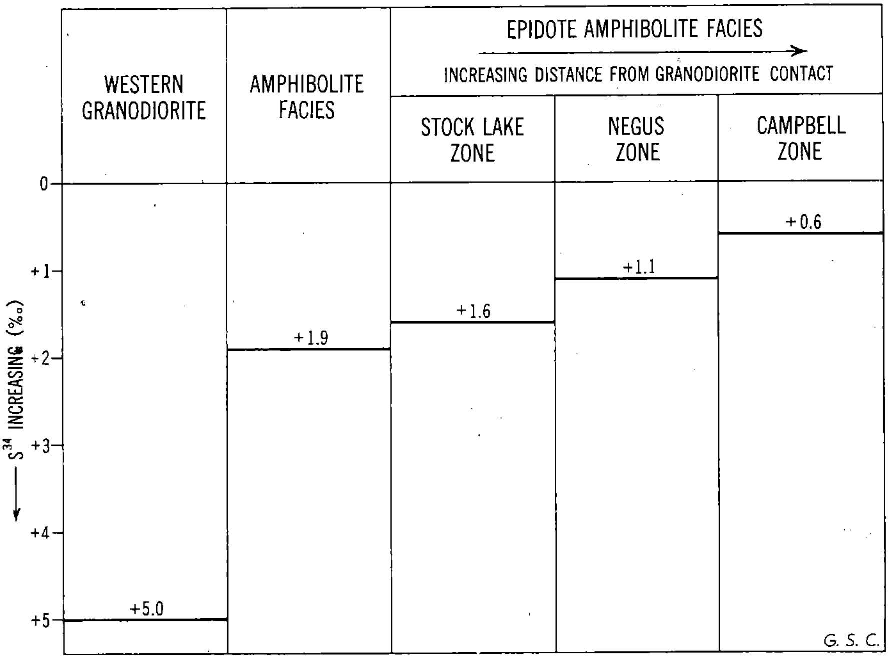

FIG. 3. Sulfur isotope distribution in granodiorite and metamorphic facies of greenstone belt.

from the Akaitcho mine (No. 104) all of the epidote amphibolite samples contain less S^{34} than the composite from the amphibolite facies.

The isotopic values are plotted according to the geographical location of the samples in Fig. 3. It is immediately apparent that a correlation exists between the sulfur isotope ratio and the distance from the granodiorite-greenstone contact. While the differences between the zones of the epidote amphibolite facies and the amphibolite facies are small, a major break in the isotope ratio occurs between the amphibolite facies and the western granodiorite. This is analogous to the break observed in the geochemical profiles at this contact (4).

Tuffs

The isotope values determined for ten samples of tuffaceous sediments are presented in Table 3. All of the graphitic types are enriched in S^{34}, whereas the values determined for the siliceous tuffs are all very close to the meteoritic standard. The explanation of this marked difference is obscure, but the high carbon content (Table 3) in the graphitic tuffs suggests that life processes may have been involved.

SULFUR ISOTOPE DISTRIBUTION IN DEPOSITS OF GREENSTONE BELT

Early Pre-ore Quartz Lenses in Tension Fractures

The formation of quartz lenses in tension fractures in the country rocks represents the first stage in the mineralization of the greenstone belt. As noted above, geochemical studies indicate that the fractures have been filled as the result of a transfer of silica from the wall rocks into the tension fractures. In Table 4 the isotope values determined for samples from two such quartz lenses are compared with the average value for the epidote amphibolite facies of the greenstone belt. In both cases, the lighter sulfur isotope has been concentrated in the fractures, indicating a preferential movement of the lighter isotope into the low pressure zones produced when the fractures were formed. The isotopic results would, therefore, appear to corroborate the secretion hypothesis postulated on the evidence from silica profiles (5).

Deposits in Transecting Shear Zones

The Con System.—Thirteen composite ore samples collected from the 250 to the 2,300-foot level of the Con mine have been analyzed isotopically. Three things are apparent from the results given in Table 5: 1) the ore contains considerably more S^{34} than reported for the greenstone rocks; 2) there is relatively little variation from level to level; 3) there is no evidence of a relationship between isotopic distribution and depth in the mine.

The Con mine is situated in that part of the epidote amphibolite facies represented by the Stock Lake analysis (Table 2, Fig. 3) for which a value of + 1.6‰ was obtained. The average value for the sulfide ore of the Con mine is + 3.8‰, indicating an increase of 2.2‰ over the associated country rock.

TABLE 4

EARLY PRE-ORE QUARTZ LENSES IN TENSION FRACTURES

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
114	Py in isolated tension fractures.*	North of Akaitcho fault	+0.3
144	Py in carbonate-epidote stringers, possibly pre-ore.	Associated with Campbell shear zone system, Negus mine.	+0.6

[1] Average of epidote amphibolite facies, see Table 2.

TABLE 5

CON SYSTEM - ORE - DEPTH PROFILE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
371	Py, asp, minor sulfs. Lens along 300'.*	250' level, shear C-4.	+4.2
374	Py, asp, minor sulfs. Lens along 150'.*	375' level, shear C-4.	+3.3
373	Py, asp, minor sulfs. Lens along 150'.*	500' level, shear C-4.	+6.2
377	Py, asp, minor sulfs. Lens along 250'.*	650' level, shear C-4.	+2.4
379	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 100'.*	800' level, shear C-4.	+3.1
380	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 200'.*	950' level, shear C-34.	+4.0
381	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 300'*.	1,100' level, shear C-4	+3.8
383	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 150'.*	1,250' level, shear C-34.	+3.6
387	Py and sulfs in grey, cherty replacement quartz. Lens along 25'.*	1,400' level, shear C-4.	+3.1
388	Py, asp, minor sulfs. Quartz-sericite schist, along 25' band.*	1,550' level, shear C-4.	+4.2
389	Py, asp, minor sulfs in quartz-carbonate-sericite schist. Along 350'.*	1,850' level, shear C-4	+2.9
390	Py in silicified sericite schist.	2,300' level, shear C-4	+4.3
391	Py in low-grade gold quartz ore.	2,300' level, shear C-4	+3.8
		Average	+3.8

TABLE 6

NEGUS-RYCON SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
117	Td in gold-quartz lens.	Surface, Negus-Rycon system.	+1.8
131	Py, asp, sulfs. Lens along 60'.*	100' level N-15 stope, Negus mine.	+2.7
53	Sb and minor sulfs.*	100' level, N-3 shear, Negus mine.	+0.2
132	Py, asp, sulfs. Lens along 110'*.	200' level N-15 stope, Negus mine.	+1.8
44	Sb and minor sulfs.*	225' level, R-54 shear, Rycon mine.	+1.1
133	Py, asp, sulfs. Lens along 100'.*	300' level N-15 stope, Negus mine.	+2.2
122	Py in quartz lens.*	300' level N-15 stope, Negus mine.	+3.6
134	Py, asp, sulfs. Lens along 70'.*	425' level N-15 stope, Negus mine.	+2.4
351	Py in mottled to black quartz. Lens along 40'.*	425' level N-3 shear, Negus mine.	+2.0
30	Sb and minor sulfs.*	450' level R-57 shear, Rycon mine.	+2.7
135	Py, asp, sulfs. Lens along 100'.*	550' level N-15 stope, Negus mine.	+0.7
137	Py, asp, sulfs. Lens along 80'.*	675' level N-15 stope, Negus mine.	+2.0
52	Massive py in gold quartz lens. Chip sample	675' level N-3 shear, Negus mine.	+0.4
51	Sp in gold quartz lens.*	675' level N-3 shear Negus mine.	+3.3
45	Sb and minor sulfs.*	800' level, Rycon mine.	+1.3
138	Py, asp, sulfs. Lens along 110'.*	800' level N-15 stope, Negus mine.	+1.3
139	Py, asp, sulfs. Lens along 80'.*	975' level N-15 stope, Negus mine.	+1.1
141	Py, asp, sulfs. Lens along 80'.*	1,100' level N-15 stope, Negus mine.	+0.7
142	Py, asp, sulfs. Lens along 20'.*	1,250' level N-15 stope, Negus mine.	+1.8
	Average	Total	+1.7
	Average	Less late minerals (Samples 117, 53, 44, 30, 45)	+1.9

The Negus-Rycon System.—A total of nineteen ore samples, listed in Table 6, were studied from the Negus-Rycon system. The ore in this system contains sulfur considerably lighter (+ 1.7‰) than that found in the Con mine (+ 3.8‰), but heavier than the neighboring epidote amphibolite facies (+ 1.1‰).

Ten of the samples were taken between the 100- and 1,250-foot levels of the N-15 stope, of the Negus mine. The results, given in Table 7, show no systematic variation with depth.

The Giant-Campbell System.—The isotope values determined for twelve samples from mines and prospects in the Giant-Campbell system are given in Table 8. A rather large spread exists between the samples studied, but the average value of + 2.5‰ is again heavier than the value of + 0.6‰ determined for the associated epidote amphibolite facies of the Campbell zone.

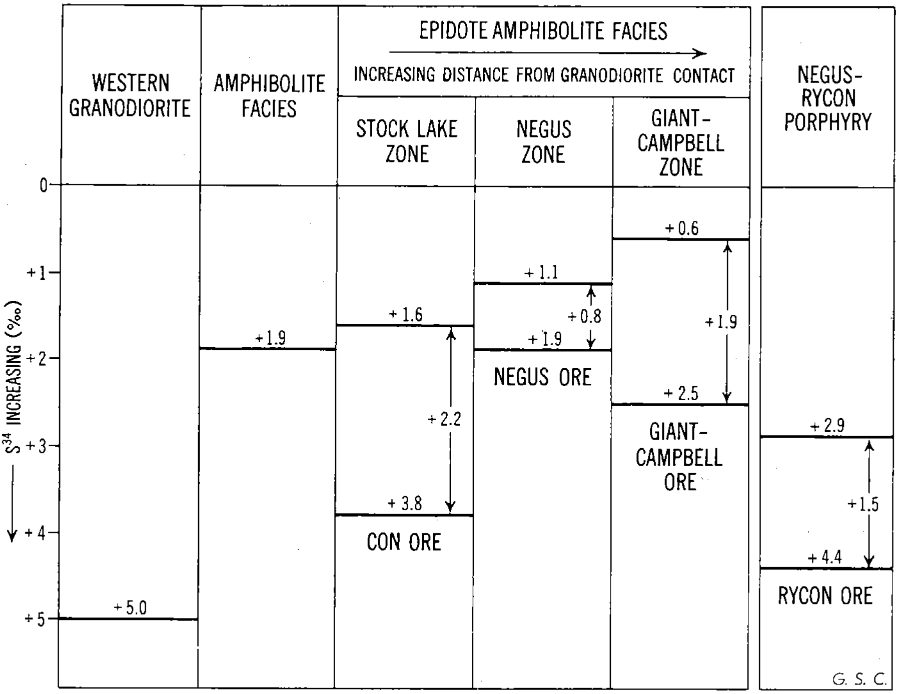

FIG. 4. Sulfur isotope distribution in gold-quartz deposits of greenstone belt.

The average results for the three systems are combined with the analyses of the country rock in Figure 4. With the exception of the Negus mine, the sulfur isotope ratios determined for the ore zones exhibit the same correlation with distance from the granite contact observed in the case of the metamorphic facies. This indicates to us that the individual orebodies contain sulfides derived by diffusion from their associated country rock and that the amount of enrichment over the country rock base level is of the same

TABLE 7

DEPTH PROFILE NEGUS MINE, NEGUS-RYCON SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
131	Py, asp, sulfs. Lens along 60'.*	100' level N-15 stope.	+2.7
132	Py, asp, sulfs. Lens along 110'.*	200' level N-15 stope.	+1.8
133	Py, asp, sulfs. Lens along 100'.*	300' level N-15 stope.	+2.2
134	Py, asp, sulfs. Lens along 70'.*	425' level N-15 stope	+2.4
135	Py, asp, sulfs. Lens along 100'.*	550' level N-15 stope.	+0.7
137	Py, asp, sulfs. Lens along 80'.*	675' level N-15 stope.	+2.0
138	Py, asp, sulfs. Lens along 110'.*	800' level N-15 stope.	+1.3
139	Py, asp, sulfs. Lens along 80'.*	975' level N-15 stope.	+1.1
141	Py, asp, sulfs. Lens along 80'.*	1,100' level N-15 stope.	+0.7
142	Py, asp, sulfs. Lens along 20'.*	1,250' level N-15 stope.	+1.8
		Average	+1.7

TABLE 8

GIANT-CAMPBELL SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
361	Py in silicified sericite schist.*	100' level Giant mine, Giant system.	+3.6
365	Py, asp, minor sulfs.*	425' level, Giant mine, Giant system.	+2.4
105	Py, asp, minor sulfs.*	310 stope Giant mine, Giant system.	+2.2
108	Py.*	Brock shear zone. Surface, Giant system.	+2.4
107	Sp, late stage.*	306 stope, Giant mine, Giant system.	+0.4
50	Sb and minor sulfs in vugs.*	Giant mine, Giant system	+0.3
39	Gn, late stage.	306 stope, Giant mine.	0.0
102	Py, asp, minor sulfs. Split core sample.	Akaitcho mine, Giant system.	+3.1
110	Py, asp, minor sulfs. Split core sample.	Lynx claim, Giant system.	+2.4
109	Py.*	North of Lynx claim.Surface. Giant system.	+1.9
126	Py, asp, minor sulfs.*	1,300' level Negus mine, Campbell system.	+1.3
369	Py, asp, minor sulfs. Lens along 500'.*	2,750' level Con Mine, Campbell system.	+3.6
	Average	Total	+2.0
	Average	Less late minerals (Samples 107, 50, 39)	+2.5

TABLE 9

PARALLEL SHEAR ZONE SYSTEMS - MINERALIZED ZONES AND ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
350	Cp and sulfs in quartz lens-ore.*	A.E.S. system, Gar Lake. Surface.	+3.2
113	Py in quartz lens-ore.*	Ranney system, Between West Bay and Akaitcho faults.	+2.9
112	Py in quartz lens-ore.*	Ranney system north of Akaitcho fault.	+0.9
54	Sp and Sb.*	Ranney system, south of Crestaurum mine.	0.0
398	Py, sulfs, sb and sp in silicified ore.*	Crestaurum system.	+2.2
399	Massive sb in ore.	Crestaurum system.	+1.6
46	Sp in ore, age uncertain, probably ore stage.	Crestaurum system.	+3.6
47	Late gn and sp.	Crestaurum system.	+0.9
395	Py in quartz lens.*	Kam Point system. Surface.	+3.6
394	Cp in quartz lens.*	Kam Point system. Surface.	+3.3
	Average	Total	+2.2
	Average	Less late minerals (Samples 54, 399, 47)	+2.8
	Average py - asp ore - Ranney-Crestaurum system		+2.4

order of magnitude in each shear zone system. The inconsistency observed in the Negus mine is believed attributable to a high abundance of paragenetically late minerals (See below).

In addition, the results obtained for the sulfides of the Negus-Rycon porphyry and the associated Rycon ore (No. 392 Table 1 and No. 366 Table 10) are illustrated in Figure 4. It will be noted that the sulfide ore is 1.5‰ heavier than the sulfides of the porphyry, an increase essentially in agreement with that reported for the Con and Giant-Campbell ores.

Deposits in Parallel Shear Zones

These shear zone systems parallel the strike and in many cases the dip of the lava flows. All shear zones sampled lie within the epidote amphibolite facies. Ten samples, taken from the A.E.S., Ranney, Crestaurum, and Kam Point systems, have been analyzed and the values determined are listed in Table 9. The average value of + 2.8‰ is again heavier than any of the ratios obtained for the epidote amphibolite facies (Table 2).

Profiles Across Major Shear Zones

The major gold-quartz orebodies and their associated alteration haloes are localized in shear zones in the greenstone belt (Fig. 1). The alteration haloes comprise a carbonate-sericite schist zone adjacent to the orebodies, which grades through a chlorite-carbonate or chlorite schist zone into the epidote amphibolite country rock. The widths of the alteration zones are variable; in places they are a few inches to a few feet in width, in other places they extend over hundreds of feet.

Where possible, composite samples representing the country rock, chlorite schist, carbonate-sericite schist, and the ore, were collected in sequence on particular mine levels, to determine whether or not an isotopic variation existed across the alteration zones. The results of eighteen profiles across both transecting and parallel systems are given in Tables 10 and 11.

In some instances, it was impossible to separate the two phases of alteration and only one isotope determination has been reported. The description indicates whether the sample represents a combination of both the chlorite and the carbonate-sericite schist or only the carbonate-sericite schist. In some shear zones it was impossible to obtain samples from the associated epidote amphibolite country rock. In such cases, the average value for the epidote amphibolite facies (+ 1.4‰) was used for comparison.

From an examination of the values obtained for the profiles, it is evident that: 1) without exception, in the eighteen cases considered, the ore contains more S^{34}—i.e. is heavier—than the associated epidote amphibolite country rock; 2) in twelve instances, the sulfur in the ore is also heavier than the sulfur in the alteration zones; 3) in five of the six cases in which the sulfur in the ore is lighter than the associated sulfur in the alteration zone, the value for the ore is within 10 percent of the heaviest member of the alteration zone.

TABLE 10

PROFILES OF TRANSECTING SYSTEMS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
Con system - Profile 1			
	Epidote amphibolite facies.[1]	Greenstone belt	+1.4
372	Py and asp in sericite schist. Along 300'.*	250' level Con mine. Shear C-4.	+3.6
371	Py, asp, sulfs - ore. Lens along 300'.*	250' level Con mine. Shear C-4	+4.2
Con system - Profile 2			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
375	Py and asp in sericite schist. Along 250'.*	650' level, Con mine. Shear C-4.	+2.0
377	Py, asp, sulfs - ore. Lens along 250'.*	650' level Con mine. Shear C-4.	+2.4
Con system - Profile 3			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
378	Py, asp in sericite schist. Along 20'.*	800' level Con mine. Shear C-4	+3.3
379	Py, asp, sulfs-ore. Lens along 100'.*	800' level Con mine. Shear C-4 .	+3.1
Con system - Profile 4			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
382	Py and asp in silicified sericite schist. Lens along 200'.*	1,100' level Con mine. Shear C-4	+4.2
381	Py, asp and sulfs in quartz-sericite schist-ore. Along 300'.*	1,100' level Con mine. Shear C-4.	+3.8
Con system - Profile 5			
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
385	Py and minor asp. Average of two samples of chlorite carbonate and chlorite-carbonate-sericite schist. Along 50'.*	1,400' level Con mine. Shear C-4.	+1.1
386	Py and asp in carbonate-sericite schist. Along 20'.*	1,400' level Con mine. Shear C-4	+2.4
387	Py and sulfs in grey cherty replacement quartz lens. Lens along 25'.*	1,400' level Con mine. Shear C-4	+3.1
Negus-Rycon system - Profile 1			
118	Py in epidote amphibolite facies. Across 50'.*	Negus-Rycon system, 300' level Negus mine.	+1.1
119	Py in chlorite schist. Across 1'.*	Negus-Rycon system, 300' level Negus mine.	+2.0
121	Py and asp in carbonate sericite schist. Across 1'.*	Negus-Rycon system, 300' level Negus mine.	+2.2
122	Py in quartz lens adjacent to No. 121. - ore.*	Negus-Rycon system, 300' level Negus mine.	+3.6
Negus-Rycon system - Profile 2			
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
353	Py and pyrr in chlorite schist. Across 6".*	Negus-Rycon system, 425' level Negus mine.	+1.8
352	Py and asp in sericite-carbonate schist. Across 2".*	Negus-Rycon system, 425' level Negus mine.	+1.6
351	Py in mottled to black quartz lens - ore. Lens along 40'.*	Negus-Rycon system, 425' level Negus mine.	+2.0

Table 10 - cont'd.

Negus-Rycon system - Profile 3			
392	Porphyry. Exposed dike.*	Rycon mine.	+2.9
65	Quartz feldspar porphyry. All bodies.*	Rycon, Con, and Negus mine areas.	+3.1
367	Disseminated py in sericitized porphyry.	5th level Rycon mine.	+4.0
366	Disseminated py in grey quartz adjacent to No. 367.	5th level Rycon mine.	+4.4
Campbell system - Profile 1			
123	Py in epidote amphibolite facies. Across 250'.*	Campbell system, 1,300' level Negus mine.	+0.6
124	Py in chlorite schist. Across 50'.*	Campbell system, 1,300' level Negus mine.	+1.3
125	Py in carbonate-sericite schist. Across 3'.*	Campbell system, 1,300' level Negus mine.	+1.1
126	Py, asp, sb and sulfs in quartz lens-ore.*	Campbell system, 1,300' level Negus mine.	+1.3
Giant system - Profile 1			
357	Py in chloritized epidote amphibolite facies. Across 20'.*	Giant system, 100' level Giant mine.	+1.3
358	Py in chlorite schist. Across 40'.*	Giant system, 100' level Giant mine.	+2.2
359	Py in chlorite-carbonate-sericite schist. Across 20'.*	Giant system, 100' level Giant mine.	+3.3
361	Py in silicified sericite schist-ore.*	Giant system, 100' level Giant mine.	+3.6
Giant system - Profile 2			
362	Py in chloritized epidote amphibolite facies. Across 100'.*	Giant system, 425' level Giant mine.	+1.6
363	Py in chlorite schist. Across 100'.*	Giant system, 425' level Giant mine.	+3.6
364	Py in carbonate-sericite schist. Across 20'.*	Giant system, 425' level Giant mine.	+2.9
365	Py, asp, sulfs-ore.*	Giant system, 425' level Giant mine.	+2.4
Giant system - Profile 3			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
106	Py and asp in chlorite and chlorite-carbonate schist.*	Giant system, 310 stope Giant mine.	+1.6
105	Py, asp, sulfs. Ore.*	Giant system, 310 stope Giant mine.	+2.2
Giant system - Profile 4			
104	Py in epidote amphibolite facies. Split drill core across 100'.	Giant system, Akaitcho mine.	+2.2
103	Py in chlorite and chlorite-sericite schist. Split drill core across 40'.	Giant system, Akaitcho mine.	+1.8
102	Py, asp, and sulfs-ore. Split drill core.	Giant system, Akaitcho mine.	+3.1
Handle Lake system			
147	Asp in aplite wall rock.	Handle Lake system.	+1.0
146	Asp in gold-quartz ore.	Handle Lake system.	+1.3
Fox Lake area			
87	Amphibolite facies. Composite.	Greenstone belt.	+1.9
148	Py in shear zone and quartz lens cutting amphibolite facies.	Fox Lake area.	+2.0
Octopus Lake area			
	Average of epidote amphibolite facies.[1]	Greenstone belt.	+1.4
264	Py in gold-quartz veins.	Octopus Lake area.	+2.7

[1] Average of epidote amphibolite values, see Table 2.

TABLE 11

PROFILES OF PARALLEL SYSTEMS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
A.E.S. system			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
347	Py in chlorite schist minor asp.	A.E.S. system, Gar Lake.	+3.3
346	Py in carbonate-sericite schist.	A.E.S. system, Gar Lake.	+3.6
350	Cp and sulfs in quartz lens-ore.	A.E.S. system, Gar Lake.	+3.2
Crestaurum system			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
396	Py in chlorite schist.*	Crestaurum system.	+1.8
397	Py in sericite schist.*	Crestaurum system.	+2.3
398	Py, sulfs, sb, and sp in silicified ore.*	Crestaurum system.	+2.2

[1] Average of epidote amphibolite values, see Table 2.

For purposes of illustration, an average has been taken of eight of the profiles which are complete, i.e. comprise four members. The averages are plotted in Figure 5. While there are some reversals between the zones in the individual profiles, the averages fall in a steady progression from the country rock, through the alteration halo, to the ore zone, with the heavier sulfur concentrated in the ore. This progression holds in the transecting systems, the parallel systems, in the Rycon porphyry, and in isolated shear zones such as those in the Handle Lake, Fox Lake, and Octopus Lake areas. It would seem to follow, therefore, that the sulfur in the ore bears a consistent relationship to the sulfur in the associated country rock as suggested previously and as shown in Figure 4.

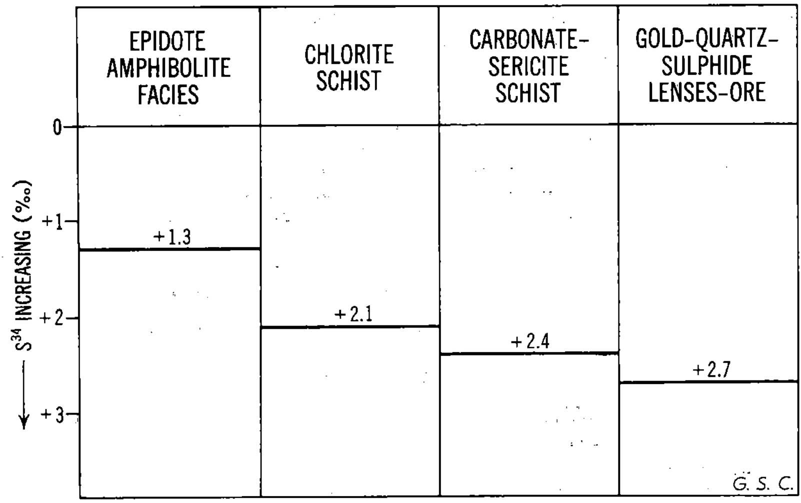

FIG. 5. Sulfur isotope distribution in alteration zones.

Paragenetic Relationships

Detailed studies (5, 9, 10) have shown that the sulfosalts, stibnite, and galena are paragenetically later than pyrite and arsenopyrite in all orebodies. In some instances, it has been possible to separate the late sulfides from the early pyrite and arsenopyrite, whereas in other cases, as in the Negus-Rycon system, for example, the desired separation was not possible.

A comparison of the sulfur isotope distribution in the early and late sulfides is given in Table 12. In all systems, the average value for the early pyrite and arsenopyrite in the ore is heavier than the average of the late sulfosalts, stibnite, and galena. The differences are most marked in the Giant-Campbell and the Ranney-Crestaurum systems where a complete separation of early and late minerals was achieved. It is apparent that the minerals formed late in the mineralization sequence have concentrated the lighter sulfur isotope, S^{32}.

TABLE 12

SULPHOSALTS, STIBNITE, AND GALENA

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
Giant-Campbell system			
50	Sb and minor sulfs in vugs.*	Giant mine.	+0.3
107	Sp, late stage.*	306 Stope, Giant mine.	+0.4
39	Gn, late stage.	306 Stope, Giant mine.	0.0
		Average	+0.2
		Average of py-asp ore[1]	+2.5
Ranney-Crestaurum system			
54	Sp and sb.*	Ranney system, south of Crestaurum mine.	0.0
399	Massive sb in ore.	Crestaurum system.	+1.6
47	Late gn and sp.	Crestaurum system.	+0.9
		Average	+0.8
		Average of py-asp ore[2]	+2.4
Negus-Rycon system			
117	Td in gold-quartz lens.	Surface.	+1.8
53	Sb and minor sulfs.*	100' level, N-3 shear Negus mine.	+0.2
44	Sb and minor sulfs.*	225' level R-54 shear, Rycon mine	+1.1
30	Sb and minor sulfs.*	450' level, R-57 shear, Rycon mine.	+2.7
45	Sb and minor sulfs.*	800' level, Rycon mine.	+1.3
		Average	+1.4
		Average py-asp ore[3]	+1.9

[1] See Table 8
[2] " " 9
[3] " " 6

TABLE 13

SECOND STAGE QUARTZ-CARBONATE LENSES - POST-ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
41	Asp in cross-cutting post-ore stringer.	2,300' level Con mine, Campbell system.	+0.7
32	Cp in post-ore quartz-carbonate lens.	2,600' level Con mine, Campbell system.	+1.6
48	Sp in post-ore fracture.	1,300' level Negus mine, Campbell system.	+0.9
49	Asp in cross-cutting quartz-carbonate lens.	1,300' level Negus mine, Campbell system.	+0.2
43	Gn, late stage.	800' level Con mine, Con system.	+1.3
39	Gn, late stage.	Giant mine, 306 stope, Giant Campbell system.	0.0
	Average		+0.8
	Average of py-asp ore - Giant Campbell system[1]		+2.5
	Average of py-asp ore - Con system[2]		+3.8

[1] See Table 8
[2] " " 5

TABLE 14

SULPHIDES IN SECOND STAGE QUARTZ-CARBONATE LENSES COMPARED WITH THOSE IN ASSOCIATED ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
49	Asp in cross-cutting quartz-carbonate lens.	1,300' level Negus mine, Campbell system.	+0.2
126	Py, asp, minor sulfs in ore.	1,300' level Negus mine, Campbell system.	+1.3
41	Asp in cross-cutting post-ore stringer.	2,300' level Con mine, Campbell system.	+0.7
391	Py and asp in low grade gold-quartz ore.	2,300' level Con mine, Campbell system.	+3.8

Post-ore Quartz-carbonate Lenses

Isolated quartz-carbonate lenses, with no associated alteration haloes, cut the ore zones of the major shear zone systems. They appear to have formed as a result of the development of dilatant zones into which material moved from the surrounding rock.

The sulfur isotope values determined for samples taken from six lenses of this type are compared, in Table 13, with the average results for the sulfide ore in the corresponding systems. The sulfides in the late lenses are consistently lighter, indicating that the lighter sulfur isotope was more mobile under the influence of the pressure gradients developed in the dilatant zones.

In some instances, it has been possible to compare the sulfur isotope ratios of sulfides in late lenses with sulfide ore in close proximity to the lenses on the same level of a mine. Two examples are given in Table 14 indicating the magnitude of the isotopic fractionation resulting from diffusion of sulfur to its present site.

The Effect of the Diabase Dikes

Diabase dikes cut the orebodies at several places. Two occurrences, one on the 375-foot level of the Con system, and the other on the 2,750-foot level of the Campbell system, were sampled in detail to test the hypothesis that the temperature gradient associated with the cooling of the molten dike modified the existing sulfur isotope distribution. As shown in Table 15 and Figure 6, the effect was indeed dramatic. The sulfide minerals adjacent to the dike have been markedly enriched in S^{34} with respect to the associated ore on the same level of the mine, indicating that the lighter isotope has been preferentially expelled from the region of higher temperature.

The amphibolite facies adjacent to the western granodiorite contains sulfides which are heavier than those of the lower grade facies. In this respect, the metamorphic effect of the western granodiorite on the greenstone rocks is analogous to the effect of the temperature gradient on the adjacent sulfide ore during the cooling of the diabase dike.

Late Faults and Fractures

Seven samples from late faults and fractures were analyzed and the results are recorded in Table 16. In this group extremes ranging from + 6.6‰ to − 8.5‰ are represented with a fairly even distribution over the intermediate range. No explanation is advanced for this divergence except to suggest that each is the result of localized processes that may or may not be related to the general sulfur isotope distribution of the region.

Sulfates in Underground Waters

Four sulfate samples extracted from underground waters flowing from fractures and faults were analyzed yielding the results given in Table 17. During the first stages of the study sulfates were converted directly to SO_2 for mass spectrometric analysis, thereby eliminating the chemical conversion

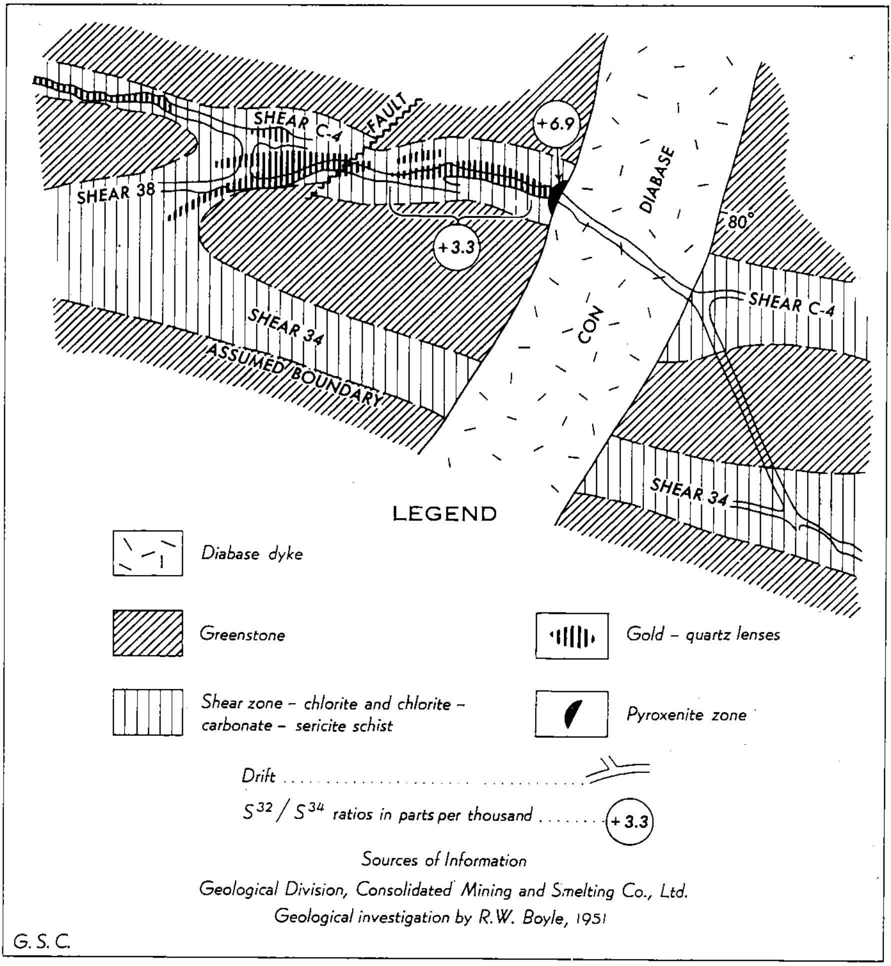

FIG. 6. Plan of geology in vicinity of diabase dike, 375 foot level, Con Mine, Con System.

from sulfate to sulfide and any possible laboratory isotope fractionation. Experience has shown, however, that reproducible results are not obtained by this procedure, and a method whereby the sulfates are converted to Ag_2S or CdS, has been adopted.

While the precision of the results for the direct conversion of $BaSO_4$ is not as high as for the conversion of the sulfides, nevertheless, the values show that all the underground waters are greatly enriched in S^{34} with respect to the sulfides in the region, and in one instance the water contains more S^{34} than sea water sulfate.

Other work (5) has suggested that the underground waters are derived from surface lakes and ponds overlying the shear zones. In these bodies

TABLE 15

EFFECT OF DIABASE DIKE - CON MINE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
Shear C-4, Con system			
374	Py, asp, sulfs. Lens along 150'.*	375' level. 100' southwest of diabase dike contact.	+3.3
262	Py from pyroxenite alteration zone.	375' level. Adjacent to dike contact.	+6.9
Campbell system			
369	Py, asp, sulfs. Lens along 500'.*	2,750' level. 500' south of dike contact.	+3.6
263	Py in quartz lens.*	2,750' level. 25' south of dike contact.	+3.8
368	Py.*	2,750' level. In shear adjacent to diabase contact.	+4.2

TABLE 16

LATE FAULTS AND FRACTURES

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
Late faults			
89	Py in late fault.*	Pud fault, Sand Lake area.	+2.9
127	Crystals of py associated with calcite.	Negus fault, 225' crosscut, Negus mine.	+1.8
88	Cp in white calcite.	Townsite fault, Latham Island.	+0.3
22	Cp in quartz.	Akaitcho fault.	-6.5
Late fractures			
24	Py in late fracture.	300' level Negus mine, Negus-Rycon system.	+6.6
23	Py in late slip.	425' level Negus mine, Negus-Rycon system.	-0.2
370	Sp in axinite vein cutting late diabase dike.	2,300' level, Con mine, Campbell system.	+1.1

TABLE 17

UNDERGROUND WATERS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
151	Sulfates precipitated from water issuing from Negus fault.	Negus mine, Campbell system.	+17.2[1]
459	Sulfates precipitated from water from fracture associated with West Bay fault.	2,300' level Con mine, Campbell system.	+ 9.1[2]
193	Sulfates from carbonate stalactite and stalagmite associated with 459.	2,300' level Con mine, Campbell system.	+11.2[1]
460	Sulfates precipitated from saline water flowing from fracture.	2,300' level Con mine, Con system.	+25.5[3]

[1] Sulfur dioxide produced directly from $BaSO_4$. See text.
[2] Sample converted to Ag_2S for conversion to SO_2.
[3] Sample converted to CdS for conversion to SO_2.

TABLE 18

YELLOWKNIFE SEDIMENTS - COUNTRY ROCKS

SAMPLE	DESCRIPTION	LOCATION	% CARBON	% SULPHUR	$\delta S^{32}/S^{34}$(‰)
96	Py from greywacke, arkose and quartzite samples[1].	Burwash area, relatively unmetamorphosed zone.	0.13	0.13	+1.6
92	Py from graphitic slate and argillite samples[2].	Burwash area, relatively unmetamorphosed zone.	0.30	0.68	+3.6
393	Py from four skarn lenses.*	Prosperous Lake area, in hornfels and highly metamorphosed zone.	trace to 0.10	0.10	+3.6
	Weighted average greywacke to slate 10:1				+1.8

[1] Composite sample of approximately 70 specimens and chips from Yellowknife sediments.

[2] Composite sample of approximately 40 specimens and chips from Yellowknife sediments.

TABLE 19

GOLD-QUARTZ DEPOSITS IN YELLOWKNIFE GROUP SEDIMENTS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
62	Composite of sp, gn and py.	Ptarmigan mine.	+0.4
63	Sp.	Ptarmigan mine.	+3.8
60	Py in vug.	Ptarmigan mine.	+2.5
61	Py in seam in quartz.	Ptarmigan mine.	+2.4
98	Gn.	In veins north of Ptarmigan mine.	+1.3
99	Sp.	In veins north of Ptarmigan mine.	+2.2
97	Sp.	Tin Can claim, Prosperous Lake.	+2.0
111	Py.	Walsh Lake.	+2.3
94	Asp and minor py in quartz vein.	Burwash mine.	+4.0
	Average		+2.3
	Weighted average greywacke to slate[1]		+1.8

[1] See Table 18

TABLE 20

PROFILE ACROSS BURWASH VEIN

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
96	Py in greywacke.*	Burwash area, relatively unmetamorphosed zone.	+1.6
95	Py and asp in wall-rock alteration zone adjacent to quartz vein.	Burwash mine.	+2.9
94	Asp and minor py in quartz vein.	Burwash mine.	+4.0

TABLE 21

REPRODUCIBILITY OF INSTRUMENTAL ANALYSES

A. Sulfide sample No. 94

Substandard No.	$\delta S^{34}/S^{32}$(‰)	Date Analysed
27	+3.8	20-3-56
27	+4.0	21-3-56
27	+4.0	22-3-56
27	+4.2	23-3-56
27	+4.0	9-4-56
27	+4.2	16-4-56
27	+4.2	16-5-56
27	+4.0	25-5-56
196	+4.0	28-6-56
	+4.0 ± 0.14**	

B. Sulfide sample No. 109

27	+1.8	6-4-56
27	+1.8	24-4-56
27	+1.8	25-4-56
27	+1.8	16-5-56
196	+1.8	12-7-56
196	+1.8	13-7-56
196	+2.0	18-7-56
196	+2.0	19-7-56
196	+2.0	22-8-56
196	+2.0	5-9-56
196	+2.2	10-9-56
196	+2.0	10-9-56
196	+2.0	10-9-56
579	+1.8	3-4-58
	+1.9 ± 0.12**	

** Standard deviation

bacteria are active, producing methane and hydrogen sulfide. In view of this, it seems probable that the heavy sulfates in the underground waters are due to the oxidation, in part bacterial, of sulfides in the shear zones and country rocks.

SULFUR ISOTOPE DISTRIBUTION IN YELLOWKNIFE GROUP SEDIMENTS

Country Rocks

Sulfur isotope ratios determined for sulfides from composite samples of the Yellowknife sediments are given in Table 18. All the sulfides in this suite of rocks contain more S^{34} than found in meteoritic troilite, and the ratios are similar to those determined for the sulfides in the amphibolites of the Greenstone belt. A notable feature is that the arkose, greywacke, and quartzite (No. 96) with a low sulfur and carbon content, contains less S^{34} than the graphitic slate and argillite composite (No. 92), which has a relatively high sulfur and carbon content. This is analogous to the relationship found between the siliceous and graphitic tuffs of the greenstone belt.

Since the ratio of greywacke to slate in the field is approximately ten to one this ratio has been used in the calculation of the weighted average (+ 1.8‰) for the sedimentary terrain. This average will be used for comparison with the isotopic values determined for sulfides in the gold-quartz lenses in these rocks.

Deposits

The isotopic values for nine samples from veins in the sedimentary area are given in Table 19. Since all mines are now inactive, no systematic collection was possible, and specimens were selected from mine dumps and surface exposures.

Although there is considerable variation from vein to vein, the isotopic values are similar to those found in the greenstone belt. All samples analyzed contain more S^{34} than found in meteoritic troilite. In addition, the average value of the ore samples is heavier than the weighted average of the greywacke and slate of the country rock.

In a single instance, at the Burwash mine, it was possible to sample systematically across the country rock and alteration zone associated with the vein. The isotopic results, given in Table 20, show that there is an enrichment in S^{34} in the sulfides as one proceeds from the country rock, through the alteration zone, to the ore, with the heaviest values localized in the ore. This distribution is identical to the distribution observed in the alteration zones associated with the orebodies in the shear zones of the greenstone belt.

SUMMARY

This investigation has revealed the following:

1. Sulfides in the western granodiorite contain more S^{34} than the sulfides in any of the other major rock units.
2. The sulfides in the quartz-feldspar porphyries are also relatively enriched in S^{34}, having isotope ratios similar to those of the sulfides in the granodiorite.

3. Sulfides in the metamorphic facies of the greenstone belt are depleted in S^{34} with respect to the sulfides of the western granodiorite. The depletion increases with distance east of the granodiorite-greenstone contact.

4. Tuffaceous rocks, high in carbon and sulfur, contain sulfides enriched in S^{34}, whereas siliceous tuffs, low in carbon and sulfur, contain sulfides depleted in the heavier sulfur isotope. Some of the lightest sulfur ratios were found in the sulfides of the siliceous tuffs.

5. Early pre-ore quartz lenses contain sulfides enriched in S^{32} compared with sulfides in their enclosing country rocks.

6. In all shear zone systems, the sulfide ore is enriched in S^{34} with respect to the sulfides in the neighboring host rocks.

7. No systematic relationship was observed between the isotopic ratio of the sulfides and depth in the mines.

8. The average values obtained for a series of profiles taken across the major alteration haloes fall in a regular progression from the host rocks through the alteration halo to the ore zone, with the heavier sulfur concentrated in the ore.

9. Sulfosalts, stibnite, and galena, which are paragenetically later than pyrite and arsenopyrite in all orebodies, are enriched in S^{32} with respect to associated pyrite and arsenopyrite.

10. Sulfides in post-ore quartz-carbonate lenses contain more S^{32} than the associated sulfide ores.

11. The sulfide minerals adjacent to post-ore diabase dikes have been markedly depleted in S^{32} with respect to sulfides remote from the dike.

12. The isotopic abundance ratios for sulfides in late faults and fractures vary over the whole range defined by this investigation.

13. All of the sulfate samples studied contain more S^{34} than found in sulfides of the region.

14. Sulfides in the Yellowknife sediments have isotopic ratios similar to those found in the amphibolites of the greenstone belt.

15. Sulfides in greywacke, arkose, and quartzites, with a low sulfur and carbon content, contain less S^{34} than sulfides in graphitic slates and argillites, which contain relatively more sulfur and carbon. In this respect the isotopic distribution resembles that found in siliceous and graphitic tuffs of the greenstone belt.

16. Sulfides from all veins in the Yellowknife sediments contain more S^{34} than meteoritic troilite, and the average value of nine ore samples is heavier than the weighted average of sulfides in the greywacke and slate.

17. A profile across the Burwash vein exhibits the same phenomenon observed in the alteration haloes associated with the orebodies of the greenstone belt.

DISCUSSION

It is assumed that the sulfides of the region originally contained the sulfur isotopes in the same proportions as found in meteoritic troilite[2] and that

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[2] This postulate seems justified since the Yellowknife sediments probably represent the initial reworking of crustal material and the greenstones (lavas) were derived from a deep-seated primordial source.

the observed distribution has resulted from the subsequent influence of temperature, pressure, and chemical gradients.

The greatest enrichment of the heavier isotope has taken place in those bodies of rock that have been subjected to the highest temperature, namely the western granodiorite, the high-grade metamorphic facies, the porphyritic bodies, and the sulfide ore adjacent to the diabase dikes.

In the western granodiorite the enrichment in S^{34} has resulted in the formation of sulfides with an isotopic ratio of + 5.0‰ heavier than meteoritic troilite. If this body of rock or its antecedent originally contained sulfur with a meteoritic isotope ratio, what has become of the lighter sulfur isotopes? There would appear to be two possible answers to this question: 1) the lighter sulfur isotope migrated into the greenstone rocks which are now found to contain more S^{32} than the western granodiorite; or 2) the lighter species has moved out of the granodiorite and has escaped, i.e. the granodiorite has been out-gassed.

If the sulfur had simply migrated from the granodiorite into the greenstone rocks two features should be observed: a) the distribution should be a smooth function across the granodiorite-greenstone contact, and b) the final overall distribution of the region should be more or less equally spaced on either side of the meteoritic base level. Neither of these distributions has been found. There is a significant break in the distribution function at the granodiorite-greenstone contact, + 5.0‰ to + 1.9‰, which is analogous to a break in the geochemical profiles reported by Boyle (4). In addition it has been shown in Figure 2 that the isotopic distribution is not equally spaced about the meteoritic level and that the overall average is heavier than meteoritic. In fact, only six samples with negative values have been found in a study embracing 140 analyses.

It is of course possible that the primary postulate is in error and that the original distribution was heavier than meteoritic, in which case, the specimens now yielding positive values in the range + 1.0‰ to + 4.0‰ may contain the lighter isotopes that originated in the granodiorite. However, the fact remains that the distribution is not continuous across the contact as would be expected if the lighter isotope had migrated from the granodiorite to its present location in the greenstone rocks. The most appealing explanation is that both the granodiorite and greenstone rocks have been out-gassed during granitization and metamorphism. In this respect, it should be noted that the rocks of the amphibolite facies adjacent to the granodiorite-greenstone contact have lost a greater percentage of the lighter sulfur isotope than those in the cooler facies, indicating that the thermal history of the rocks has been responsible for the observed isotopic distribution.

Further evidence in support of the conclusion that thermal gradients may be responsible for the preferential diffusion of the lighter isotope away from the higher temperature zones is to be found in a consideration of the sulfides adjacent to the diabase dikes. In both of the cases studied the lighter isotope has migrated away from the zone adjacent to the dike thereby causing the sulfides in the hotter zone to become markedly enriched in the heavier sulfur isotope.

Pressure gradients have also been responsible for the modification of the isotopic distribution. Sulfides in isolated lenses filling tension fractures in the epidote-amphibolite facies always contain more S^{32} than sulfides in the enclosing country rocks, indicating that the lighter isotope has been more mobile. Identical relationships have been observed in post-ore quartz-carbonate lenses.

During the formation of the large gold-quartz orebodies, pronounced chemical and pressure gradients existed, resulting in the formation of marked alteration zones about the gold-quartz lenses. From this investigation it is evident that the heavier sulfur isotope has been retained to a greater extent in the zones that have undergone extensive chemical change, and that large quantities of S^{32} diffused up the shear zone systems to the surface, thereby producing the observed sulfur isotope profiles from the country rock to the ore. As shown in Figure 4, the average values for the sulfide ore bear a relationship to the country rock in which the shear zones occur, suggesting that the sulfur now found in the orebodies originated in the associated country rocks. The magnitude of the sulfur isotopic enrichment has been found to be approximately the same in each of the transecting systems investigated.

The sedimentary area east of Yellowknife Bay was not studied in comparable detail, but the results available show that the isotope ratios have been modified in a similar manner and to a comparable degree. The orebodies, once again, contain sulfides enriched in S^{34} with respect to the greywackes and slates in which they occur. A single profile across the country rock, and alteration zone at the Burwash mine exhibits the same gradual enrichment in S^{34} as one approaches the ore. It has also been noted that the slates, which contain more graphite, contain sulfides with more S^{34} than the greywackes in which the graphite content is extremely low. This relationship is analogous to that observed for the graphitic and siliceous tuffs of the greenstone belt.

CONCLUSIONS

1. The original sulfur isotopic distribution of the region (assumed to be meteoritic) has been modified by the temperature gradient existing during granitization and metamorphism. Rock units that have had high thermal histories (western granodiorite, porphyries, diabase dikes) all contain, or are associated with, sulfides that have been enriched in S^{34}.

2. Sulfides in dilatant zones and post-ore tension fractures contain more S^{32} than sulfides in their enclosing rocks, indicating that pressure gradients have been responsible for the differential migration of the lighter sulfur isotope.

3. Under conditions of intense chemical activity, existing during the formation of the large gold-quartz orebodies and their associated alteration haloes, the heavier sulfur isotope was preferentially retained in the regions of greatest activity (the ore zones) creating the sulfur isotopic profiles observed between the country rock and ore zones.

4. The enrichment of the S^{34} has been found to be of the same order of magnitude in each of the major shear zone systems, indicating that each

system developed from the base level found in the associated metamorphic facies, and that the sulfides now found in the ore zones probably originated in the associated country rocks.

5. Graphitic tuffs contain sulfides enriched in S^{34} compared to the carbon-free siliceous types. A similar, though less marked relationship exists between slates and greywackes in the Yellowknife sediments. It is suggested that life processes may have been responsible for the enrichment of S^{34} in the graphitic rocks.

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May 6, 1960

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APPENDIX

Experimental Procedures

Conversion of Sulfide Minerals to Sulfur Dioxide.—The apparatus, illustrated in Figure 7, was employed for the conversion of sulfide samples to sulfur dioxide for mass spectrometric analysis. The quartz combustion tube, generally used by other workers, was replaced by a high temperature Leco[3] furnace. This modification was incorporated to permit combustion of sulfides above the dissociation temperature of SO_3, thereby eliminating possible fractionation of the sulfur isotopes between the SO_2 and SO_3 molecular species. The sample (approximately 100 mg of pyrite or equivalent weight of other sulfide mineral) was mixed with an equal weight of pure tin pellets to accelerate the combustion, and placed in a sulfur-free combustion boat. The oxygen used for all conversions was drawn from the same cylinder, thereby ensuring a constant oxygen isotope distribution.

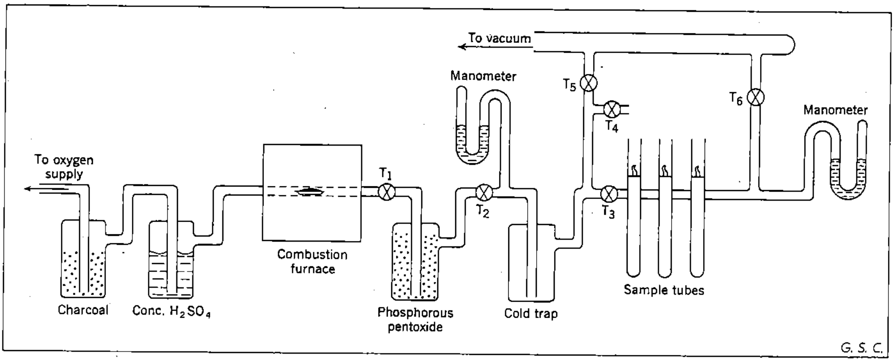

FIG. 7. Sulfur dioxide extraction and purification line.

The oxygen, after purification by passage through an activated charcoal trap, maintained at dry ice temperature, and concentrated H_2SO_4, was allowed to flow through the combustion tube and extraction line for some minutes

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[3] Leco #2600—Laboratory Equipment Corporation, St. Joseph, Michigan.

before the sample was placed in the furnace. During this period stopcocks T_1, T_2 and T_4 were open; T_3, T_5 and T_6 were closed. Stopcock T_1 was then closed, the sample boat was placed in the furnace, and a cobalt glass combustion tube window was inserted into the end of the tube to permit observation of the reaction. As gases evolved the oxygen pressure was adjusted to prevent the flow of H_2SO_4 into the charcoal trap. After a combustion period of three to four minutes the gases were condensed in the cold trap maintained at the temperature of liquid oxygen, excess oxygen being allowed to escape via T_4. When all of the combustion products were swept from the furnace, T_1 and T_4 were closed, T_5 was opened and the residual gas was transferred from the P_2O_5 trap to the cold trap. T_2 and T_5 were then closed and the liquid oxygen on the cold trap was replaced by a mixture of acetone and dry ice. At this temperature CO_2 and other volatile impurities were released, and the resulting pressure was indicated on the manometer. The volatile gases were then exhausted via T_5. The purified SO_2 was then transferred, via T_3, to an evacuated sample tube maintained at the temperature of liquid nitrogen. After all of the gas was transferred, T_3 was closed, the liquid nitrogen was removed from the sample tube and the gas was permitted to expand into the line. An estimate of the quantity of gas produced and hence the yield of the combustion was obtained from the pressure indicated on the manometer. The combustion was considered to be satisfactory when the yield indicated conversion of 95% of the sulfur to sulfur dioxide. The gas sample was then condensed into the sample tube and sealed off for transfer to the mass spectrometer. Experience has shown that eight to ten sulfide conversions may be satisfactorily carried out per day.

Conversion of Sulfates to Sulfur Dioxide.—Since the sulfur isotopes may be fractionated in laboratory chemical processes our original plans called for the direct conversion of sulfate sample materials to sulfur dioxide. It was hoped that the temperature produced in the furnace would be sufficiently high to dissociate completely the SO_4 molecules and that the oxygen supplied for the combustion would completely replace the oxygen liberated. In practice, however, we found that replicate combustions of the same sulfate sample did not yield reproducible sulfur isotope ratios. Preliminary conversion of sulfate to silver sulfide or cadmium sulfide was therefore carried out employing the method reported by Rafter (19).

Instrumental Analyses.—The isotopic analyses are reported as permil deviations from a sample of meteoritic troilite[4] which has been assigned a value of 0.0‰. The permil values are calculated from the relationship:

$$\delta S^{34}‰ = \frac{S^{34}/S^{32}\ (\text{Standard}) - S^{34}/S^{32}\ (\text{Sample})}{S^{34}/S^{32}\ (\text{Standard})} \times 1000$$

Positive values indicate an excess of S^{34} with respect to the meteoritic standard while samples enriched in S^{32} have negative values.

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[4] Troilite from a sample of "Merceditas," a medium octrahedrite, found at Chanaral, Atacama, Chile.

Simultaneous collection techniques (27) were employed for all sulfur isotope analyses. A two-litre bulb containing purified SO_2 produced from a large pyrite sample, arbitrarily chosen as a substandard, was permanently attached to one of the two sample handling lines of the mass spectrometer. A small volume of this gas was admitted to the instrument for each group of analyses, the residue being pumped away when the analyses were completed. One of the samples previously analyzed was re-analyzed with each new group, thereby providing a day to day check on the composition of the substandard and on the instrumental operation.

The results of replicate analyses carried out on two samples over a period of some months are given in Table 21. It will be noted that the standard deviation of the average of the replicate analyses is less than 0.2‰.

The isotopic results given in Table 21 also reflect the reproducibility of the conversion of sulfide minerals to sulfur dioxide. Substandard samples numbers 27, 196 and 579 represent SO_2 conversions from the same pyrite sample over a period of two years. Variations for the substandards are of the same order of magnitude as found for replicate instrumental analyses from day to day.

DIFFERENCES BETWEEN BARREN AND PRODUCTIVE INTRUSIVE PORPHYRY[1]

BRONSON STRINGHAM

ABSTRACT

It has been statistically shown that a great majority of the larger Cretaceous and younger hydrothermal ore deposits of Au, Ag, Cu, Pb, Zn, Mo, Hg, and U in the Basin and Range Province are associated with intermediate to acidic intrusive aphanitic or porphyritic rocks of near similar age. Recent work indicates that, except for the Pacific Coast Ranges and the Mother Lode area, similar ore-porphyry relationships apply to deposits over the entire western U. S. However, many intrusive porphyries exist that have little or no associated hydrothermal deposits. Some intrusive porphyries, therefore, seem to be genetically related to ore deposits while others are not. These then may conveniently be classified into 2 categories as barren and productive.

To aid further the ore finder, an attempt is made here to offer criteria that will serve to distinguish barren from productive porphyries.

Among the many suggestive distinctions the following seem to be of most importance. Productive acid porphyry bodies generally are of considerable size and seem to cross cut enclosing rock structures with very little or no disturbance due to intrusive action. On the other hand barren porphyries may be of various sizes but on the whole have a tendency to either be concordant with wall rock structures or, where cross cutting relations exist, show obvious intrusive structural effects such as brecciation, folding, or up arching. Other criteria are listed in order of importance in Table II of the paper.

INTRODUCTION

THE close areal relationship of Cretaceous or later intrusive porphyries to larger hydrothermal deposits of Pb, Zn, Au, Ag, Cu, Mo, Hg, and U of similar age in the Basin and Range Province, was statistically shown in a recent paper (17). During the past year this study has been expanded to cover all of the larger hydrothermal deposits of similar nature occurring in the entire western United States. The results of this work was presented before the A. I. M. E. at Moab, Utah in May, 1959. The statistics of the porphyry-ore relationships throughout the West as a whole turned out to be so similar to the first study of the Basin and Range Province that an independent report is not now contemplated.

The term hydrothermal is used here in the sense of magmatic hydrothermal of Jensen (8), thus the sandstone type uranium deposits of the Colorado Plateau and Wyoming have been excluded since considerable controversy exists regarding their origin. This relationship then leads to the conclusion that when exploring for similar types of hydrothermal deposits of the metals

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[1] Assistance has been received from the Kennecott Research Fund and the University Research Fund, University of Utah.