ECONOMIC GEOLOGY

AND THE

BULLETIN OF THE SOCIETY OF ECONOMIC GEOLOGISTS

VOL. 65 JANUARY–FEBRUARY, 1970 NO. 1

Sulfur Isotope Investigation of the Lead-Zinc-Silver-Cadmium Deposits of the Keno Hill-Galena Hill Area, Yukon, Canada

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Abstract

Sulfur in the sulfides of the sedimentary rocks of the Keno Hill-Galena Hill area, Yukon, Canada is relatively enriched in S^{34} compared with sulfides in the lead-zinc-silver-cadmium lodes. These data support the thesis that during diffusion of the sulfur from the country rocks the lighter S^{32} isotope was selectively concentrated in the sulfide deposits.

The sulfur isotope ratio of supergene sulfates in the oxidized zones of the deposits reflects the ratio in the hypogene sulfides. Similarly, the ratio in the sulfate of the waters leaching mineralized zones reflects the ratio in the ores, a fact that may be useful in hydrogeochemical prospecting in the area.

Introduction

THIS paper presents sulfur isotope data obtained for the deposits and country rocks of the Keno Hill-Galena Hill area of the Yukon. The study is a part of an extensive geochemical investigation of the mineralized belt that has as its aim the elucidation of the genesis of the ores.

The Keno Hill-Galena Hill deposits are situated in Central Yukon 35 miles northeast of Mayo and some 220 miles due north of Whitehorse. The lead-zinc-silver-cadmium lodes of the area, first discovered in 1913, have been prolific producers. The principal producing mines of the area (Fig. 1) are the Hector-Calumet, Elsa, and No Cash on Galena Hill and the No. 6 and No. 9 on Keno Hill. Former producing mines were the Silver King, Bermingham (Arctic and Mastiff), and Galenko on Galena Hill; the Onek, Ladue-Sadie-Friendship, Lucky Queen, and Shamrock on Keno Hill; and the Bellekeno on Sourdough Hill.

Geology and Mineralogy of the Deposits

The following briefly summarizes the salient geological and mineralogical features pertinent to the discussion of the isotopic geochemistry of sulfur. Detailed accounts are presented in publications by Carmichael (1957), McTaggart (1960), and Boyle (1965).

The consolidated rocks in the Keno Hill-Galena Hill area (Fig. 1) are mainly sedimentary in origin and include graphitic, chloritic, and sericitic schists and phyllites, thick- and thin-bedded quartzites, argillites, and a few limestone beds and lenses, all probably of late Pre-Cambrian or early Paleozoic age.[1] Conformable greenstone lenses and sills occur in profusion in places, and a few lamprophyre and quartz-feldspar porphyry dykes and sills are present locally. Granitic stocks and small plugs outcrop northwest and southeast of the main mineral belt. These masses range in composition from granodiorite to quartz diorite and appear to be intrusive into the metasediments. K/Ar age measurements of 81 and 85 m.y. based on biotite have been obtained for two granitic intrusive bodies west of Galena Hill (sample numbers G.S.C. 65-49, 65-50),[2] and a muscovite from the sedimentary chlorite-sericite schist on Galena Hill has been dated at 84 m.y. (sample number G.S.C. 65-46).[2] These ages suggest that the intrusion of the granitic bodies and the accompany-

[1] The age of these rocks is thought to be late Palaeozoic or Mesozoic by some geologists (Green and Roddick, 1962).

[2] Details of the age determinations are given in Wanless et al. (1967).

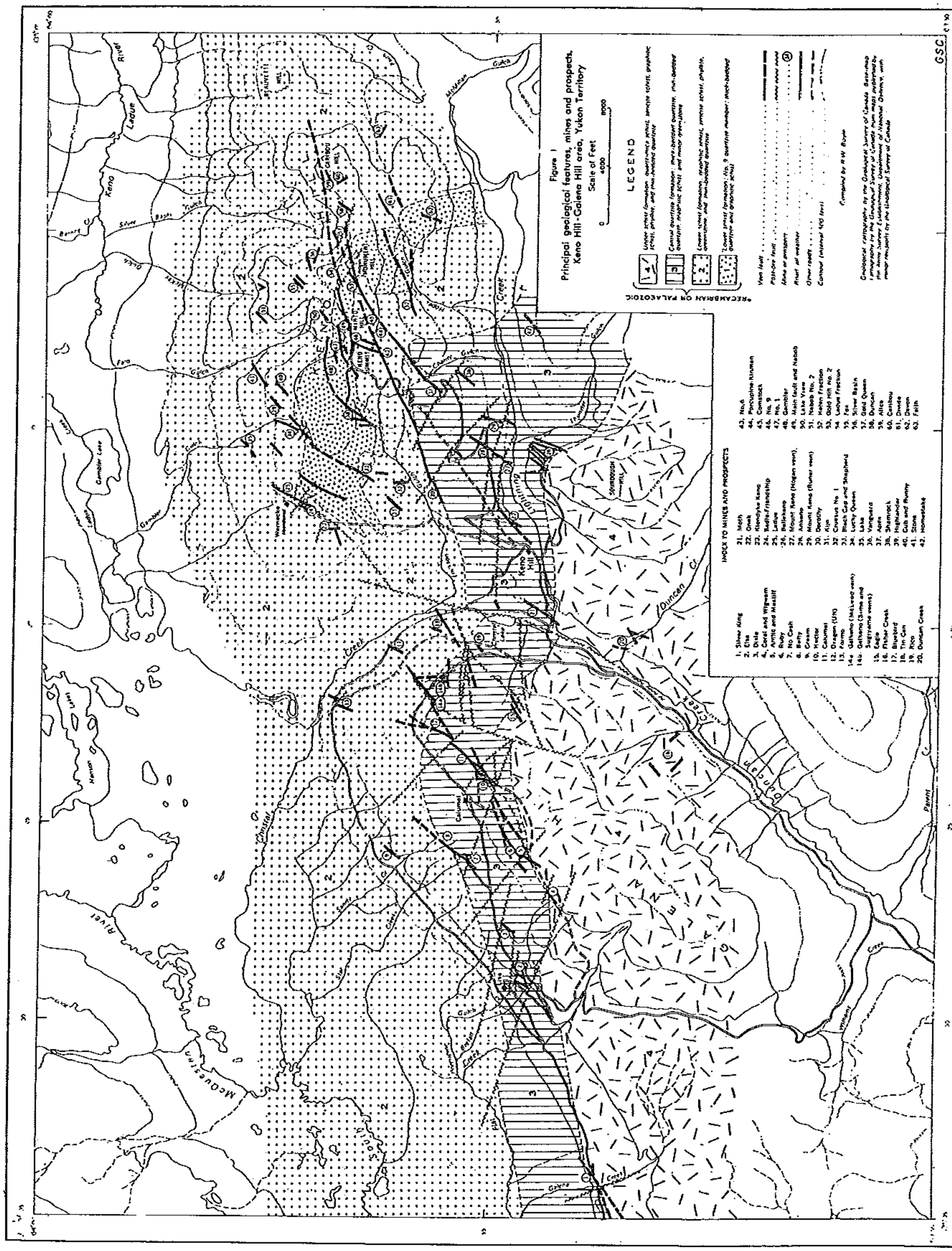

Figure 1
Principal geological features, mines and prospects, Keno Hill-Galena Hill area, Yukon Territory

ing metamorphism and deformation giving rise to the schists culminated in mid-Upper Cretaceous time. Since the ore deposits are localized in vein faults cutting and displacing the granitic rocks and schists the age is a maximum limit for the time of ore deposition.

Most of the meta-sedimentary rocks and associated greenstone sills fall into the greenschist facies. Near granitic bodies, hornfels, biotite schists, staurolite schists, garnet schists, and skarn lenses are developed, the latter chiefly from limestones and calcareous quartzites and schists.

Three major periods of hypogene mineralization are represented in the area. In sequence from oldest to youngest, these are:

The first is marked by the development of numerous quartz stringers, lenses, and irregular bodies in fractures, joints, small faults, drag folds, and contorted zones in the various types of rocks, including the greenstones. In the meta-sediments, some pyrite and a few carbonates accompany the quartz; in the greenstone rocks, epidote, chlorite, and carbonates are present in the quartz bodies. Near the granitic masses some scheelite and wolframite occur in small quartz stock-works in the sediments, and cassiterite is present in small impregnation zones in schists and phyllites. The skarn lenses referred to above were also probably formed during this period. Some of these carry scheelite, minor sulfides, and a little gold. Most of the deposits of this period are not economic.

The second period is represented by quartz-pyrite-arsenopyrite veins and lenses containing a little gold and small amounts of galena and sphalerite. These occur principally in northeast-striking vein faults that cut all rocks including apophyses of the large granitic bodies and dykes of quartz-feldspar porphyry. A few of the deposits of this period are economic.

The third period of mineralization is represented by large economic siderite lodes containing essentially sphalerite, galena, pyrite, chalcopyrite, and freibergite. These lodes occur in the reopened northeast-striking vein faults and in variously oriented subsidiary vein faults.

A north-northeast to northwest trending series of late faults cut all types of deposits in the area. These late faults are essentially barren.

There is no marked wall rock alteration associated with the veins in the sedimentary rocks. Where the veins intersect greenstones, these rocks are slightly carbonatized, chloritized, and sericitized for a few inches adjacent to the veins.

The quartz-pyrite-arsenopyrite veins and the siderite lodes are oxidized to depths varying from 20 to 600 feet. In some siderite lodes the zones of oxidation grade into the hypogene zones through zones of reduction varying from 2 to 20 feet in thickness; in others the zones of oxidation grade imperceptibly into the hypogene zones. During the oxidation of the lodes and their enclosing rocks, residual deposits and placers containing gold, scheelite, and wolframite were formed in the soils and weathered residuum in the vicinity of their respective hypogene deposits and in nearby streams.

The principal hypogene minerals in the early quartz-pyrite-arsenopyrite veins are quartz, pyrite, arsenopyrite, boulangerite, jamesonite, bournonite, and minor amounts of galena and sphalerite. In the siderite lodes, siderite, quartz, galena, sphalerite, pyrite, chalcopyrite, and freibergite predominate. Less common are, barite, pyrrhotite, stibnite, boulangerite, jamesonite, stephanite, and polybasite. Galena, sphalerite, and freibergite are the principal economic minerals in the siderite lodes.

The principal supergene minerals in the oxidized zones of the quartz-arsenopyrite and siderite lodes are limonite, wad (manganese oxides), quartz, calcite, cerussite, smithsonite, anglesite, gypsum, beudantite, scorodite, bindheimite, malachite, azurite, native silver, and pyrargyrite. Less abundant supergene minerals are pharmacosiderite, jarosite, rozenite, gunningite, senarmontite, various clay minerals, serpentine, native sulfur, and native zinc. Acanthite, covellite, galena, sphalerite, hawleyite, marcasite, pyrite, native silver, and pyrargyrite are the principal supergene minerals in the zones of reduction of the lodes. Native silver and pyrargyrite are economic minerals in some lodes.

Paragenetic Sequence in the Sulfide Deposits

As stated above the sulfides in the economic vein deposits were deposited during two principal periods of mineralization. The early period is marked by quartz veins containing pyrite and arsenopyrite with a little gold and minor amounts of galena, sphalerite, and sulfosalts, including boulangerite, jamesonite, and bournonite. The late and most important period is represented by siderite lodes containing abundant pyrite, galena, sphalerite, freibergite, and chalcopyrite with small amounts of arsenopyrite, boulangerite, jamesonite, bournonite, and pyrargyrite. Barite is the only hypogene sulfate noted in the deposits; its occurrence in the siderite lodes is sporadic and minor.

The paragenetic sequence of the sulfides and sulfosalts is complex, and there has been considerable repetition and overlapping in the precipitation processes. Disregarding minor details, the sequence in the quartz-arsenopyrite veins is: pyrite and arsenopyrite which are nearly contemporaneous, followed in turn by sphalerite, galena, and the various sulfosalts. In the siderite lodes the pyrite and arseno-

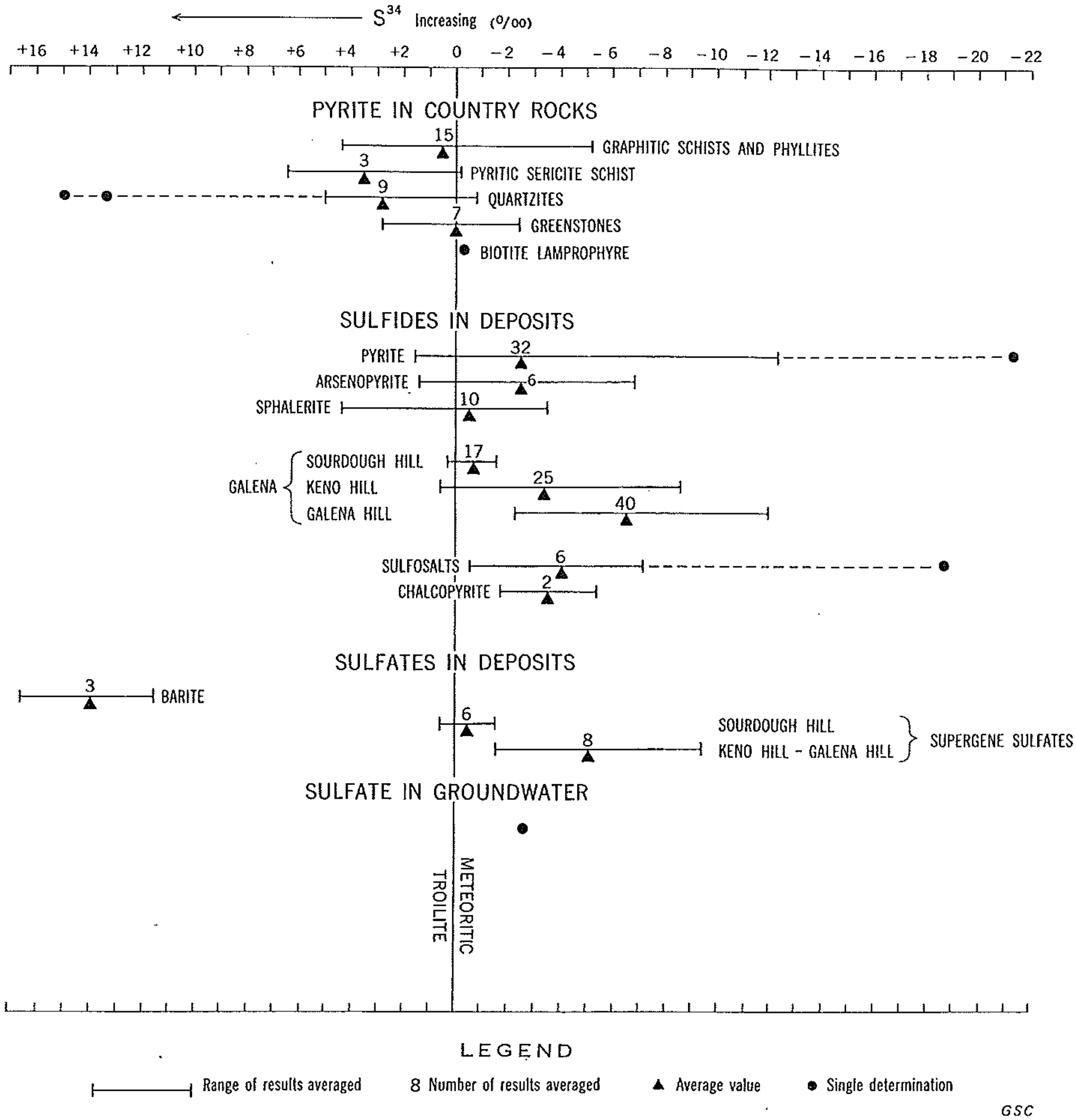

Figure 2. Sulfur isotope distribution in country rocks and deposits, Keno Hill - Galena Hill area, Yukon Territory

pyrite are nearly contemporaneous and are followed in turn by sphalerite, galena, freibergite, sulfosalts, and chalcopyrite. The last three are probably nearly contemporaneous, and there is much overlapping in the deposition sequence of galena and sphalerite. Barite, where present, is a late hypogene mineral and appears to have been precipitated after the sulfides and sulfosalts.

The principal sulfates and basic sulfates in the oxidized parts of the deposits are anglesite, beudantite, gypsum, and various iron and zinc sulfates. The anglesite originated directly by the oxidation of galena and generally incrusts this hypogene sulfide. The beudantite was derived mainly from the constituents of galena, freibergite, pyrite, and arsenopyrite by complex hydrolytic processes. The gypsum and various iron and zinc sulfates have been precipitated from downward percolating ground waters which obtained their sulfate component mainly from the oxidation of pyrite and sphalerite.

Sulfur Isotope Distribution in the Country Rocks

The sediments contain the most sulfur (avg. 0.67%), smaller amounts are found in the greenstones (avg. 0.08%), and very low concentrations are present in the granitic rocks (avg. 0.01%). Sulfide samples from the sediments and greenstones of the country rock were analyzed isotopically; the granitic rocks yielded insufficient quantities of sulfides for isotopic analysis. Experimental procedures are described in Wanless, Boyle, and Lowdon (1961).

Sedimentary Rocks.—Most of the sulfur in the sedimentary rocks is present as a constituent of pyrite, and only minor amounts occur in random specks of chalcopyrite, pyrrhotite, and sphalerite. The pyrite is most abundant in the graphitic schists and phyllites and in the black quartzite members of the sedimentary assemblage. The manner of occurrence and widespread distribution of the pyrite in these sedimentary rocks suggests that it is of syngenetic sedimentary origin, formed by the fixation of iron by H_2S, probably of bacterial origin. It has, however, been recrystallized and occurs in its present form as individual crystals, crystal groups, and fine disseminations in the schists and quartzites. Some pyrite in pure white quartzite beds occurs in fractures. This pyrite appears to have been introduced into the white quartzites, probably from interbedded pyritic schists.

The pyrite concentrates from the sediments were prepared for isotopic analysis by crushing and superpanning composite samples comprising fifty pounds of fresh rock chips selected from sites remote from the sulfide veins. The results of the isotopic analyses of the pyrite from the graphitic schist and phyllite, pyritic sericite schist, and quartzites are given in Table 1 and compared in Figure 2. The range and averages of the various groups of sediments are shown in Table 13. It will be noted that there is considerable variation in the isotopic values within the groups, but the average values all indicate enrichment in S^{34} with respect to meteoritic troilite. The reasons for the marked differences in the sulfur isotopic values between the sedimentary types are obscure. They may be related to isotopic variations in the initial sulfur contributed to the sedimentary basin, or to bacterial processes which may have given rise to the sulfur of the pyrite. With respect to the latter it is interesting to note that the pyrite in the sediments which exhibit the largest amount of organic (bacterial) activity, as witnessed by the abundance of carbon or graphite (the graphitic schists and phyllites), contains the most S^{32}. This is in agreement with the observation that sulfate reducing bacteria produce H_2S which is enriched in S^{32} with respect to the source sulfate.

Greenstones and Lamprophyre.—All of the sulfur in the greenstones and lamprophyre is present in pyrite which occurs as individual crystals, crystal groups, and irregular disseminations. Probably most

TABLE 1

SULFUR ISOTOPIC COMPOSITION OF SULFIDES (98% PYRITE) IN COUNTRY ROCKS

Laboratory number	Location and Description	δS^{34}‰
Graphitic schist and phyllite:		
51644	Near Mount Keno mine, Keno Hill; graphitic schist.	- 2.22
5783	Near Keno Hill; graphitic schist.	- 0.44
5786	Near Sadie-Friendship mine, Keno Hill; graphitic phyllite.	+ 0.89
5791	Near Sadie-Friendship mine, Keno Hill; graphitic phyllite and slate.	+ 4.44
5806	Near Klondyke-Keno mine, Keno Hill; graphitic schist and phyllite.	+ 1.11
5807	Near Klondyke-Keno mine, Keno Hill; phyllite and thin-bedded quartzite.	- 4.0
5808	Near Klondyke-Keno mine, Keno Hill; graphitic schist and phyllite.	+ 2.0
5794	Near Formo prospect, Galena Hill; graphitic schist.	+ 1.33
5795	Near Formo prospect, Galena Hill; graphitic schist.	- 2.44
5797	Hector-Calumet mine area, Galena Hill; graphitic schist and phyllite.	+ 3.33
5746	Hector-Calumet mine area, Galena Hill; graphitic phyllite and schist.	+ 1.56
5750	Hector-Calumet mine area, Galena Hill; graphitic schist.	- 0.56
5758	Hector-Calumet mine area, Galena Hill; graphitic schist.	+ 3.78
5756	Cream prospect area, Galena Hill; graphitic schist and phyllite.	+ 3.78
5757	Flat Creek area, Galena Hill; graphitic schist and phyllite.	- 5.11
	Average	+ 0.63
Pyritic sericite schist:		
5785	Sadie-Friendship mine area, Keno Hill.	- 0.22
5792	Galkeno mine area, Galena Hill.	+ 4.22
5802	Hector-Calumet mine area, Galena Hill.	+ 6.44
	Average	+ 3.48
Quartzites:		
5779	Near Mount Keno mine, Keno Hill; thin-bedded quartzite.	+13.33
5787	Near Sadie-Friendship mine, Keno Hill; thin-bedded quartzite and phyllite.	+ 3.11
5788	Near Sadie-Friendship mine, Keno Hill; thin-bedded quartzite and phyllite.	+ 3.11
5741	Hector-Calumet mine area, Galena Hill; thin-bedded graphitic quartzite.	+ 4.67
5799	Hector-Calumet mine area, Galena Hill; thin-bedded graphitic quartzite.	+ 3.00
51637	Hector-Calumet mine area, Galena Hill; thin-bedded quartzite and phyllite.	+ 2.67
5803	Hector-Calumet mine area, Galena Hill; thin-bedded quartzite.	+ 2.67
5744	Hector-Calumet mine area, Galena Hill; thin-bedded quartzite.	+ 5.00
5748	Hector-Calumet mine area, Galena Hill; grey quartzite.	+ 2.67
5751	Hector-Calumet mine area, Galena Hill; medium- and thin-bedded quartzite.	- 0.89
5752	Hector-Calumet mine area, Galena Hill; thin-bedded quartzite and phyllite.	+14.89
	Average (less 5779 and 5752)	+ 2.89
Greenstones:		
51635	Near Keno Hill townsite; massive diabasic greenstone.	+ 2.32
5778	Ankeno prospect area; schistose greenstone.	+ 1.33
5780	Mount Keno prospect area; massive greenstone.	- 0.67
5781	Mount Keno prospect area; sheared greenstone.	+ 2.89
5605	Galkeno mine area; massive greenstone from drill core.	- 0.44
Greenstones (continued):		
5737	Hector-Calumet mine area; relatively unaltered greenstone.	- 1.56
5738	Hector-Calumet mine area; altered greenstone.	- 2.44
	Average	+ 0.03
Biotite Lamprophyre:		
5796	Formo prospect area; pyritiferous lamprophyre.	- 0.22

TABLE 2

SULFUR ISOTOPIC COMPOSITION OF PYRITE IN DEPOSITS

Laboratory number	Location and description	δS^{34}‰
S809	Bellekeno vein system, Sourdough Hill; botryoidal.	-21.11
S810	Bellekeno vein system, Sourdough Hill; massive.	+ 1.11
S812	Bellekeno mine, Sourdough Hill; cubic.	+ 1.56
S811	Bellekeno mine, Sourdough Hill; massive.	+ 1.11
S762	Mount Keno prospect, Keno Hill; massive.	- 6.67
S813	Onek mine, Keno Hill; cubes.	+ 0.22
S815	No. 6 vein system, Keno Hill; massive.	+ 0.67
S816	Klondyke-Keno prospect, Keno Hill; E-W vein, massive.	- 6.44
S817	Klondyke-Keno prospect, Keno Hill; N-S vein, cubic.	- 3.55
S818	Moth prospect, Keno Hill; cubic.	- 0.22
S819	Sadie-Friendship mine, Keno Hill; massive.	- 4.44
S821	Galkeno mine, Galena Hill; massive.	- 0.67
S775	Galkeno mine, Galena Hill; massive.	- 1.11
S822	Formo prospect, Galena Hill; massive; mean of three bulk samples.	- 9.40 (± 0.50)
S831	Hector-Calumet mine, Galena Hill; 100 foot level, massive.	- 3.33
S826	Hector-Calumet mine; 300 foot level, massive.	- 1.78
S835	Hector-Calumet mine; 400 foot level, cubic.	- 0.89
S836	Hector-Calumet mine; 400 foot level, cubic.	- 2.00
S837	Hector-Calumet mine; 525 foot level, massive and cubic; two composite samples.	- 2.67
S840	Hector-Calumet mine; 525 foot level, massive and cubic.	- 3.11
S841	Hector-Calumet mine; 650 foot level, cubic.	- 2.44
S843	Hector-Calumet mine; 650 foot level, massive.	- 2.22
S764	Hector-Calumet mine; 650 foot level, massive.	-12.22
S765	Hector-Calumet mine; 775 foot level, cubic.	- 2.44
S771	Hector-Calumet mine; 775 foot level, cubic and massive.	- 2.67
S772	Hector-Calumet mine; 900 foot level, cubic and massive.	- 0.67
S768	Hector-Calumet mine; 900 foot level, massive.	- 3.11
S774	Hector-Calumet mine, 1165 foot level, massive and cubic.	- 2.44
S753	Silver King mine, Galena Hill; in quartzite.	+ 0.56
S754	Silver King mine, Galena Hill; in seams in quartzite.	- 1.11
S755	Silver King mine, Galena Hill; massive.	- 7.56
S760	Dublin Gulch area; massive in breccia zone.	+ 1.45
S761	Dublin Gulch area; massive in breccia zone.	- 1.78
	Average (less S809)	- 2.45

of the pyrite in the greenstones is syngenetic and crystallized from a diabasic magma, although during alteration of the diabase and gabbro sills to greenstone, some sulfur may have been introduced from the enclosing sediments. As shown in Tables 1 and 13 and Figure 2 the range in the sulfur isotopic values for pyrite in the greenstones is small, with an average close to the meteoritic standard. Some of the isotopic variation may be due to the suggested sedimentary sulfur component; this hypothesis is supported by the results of chemical studies carried out on altered and unaltered diabase and gabbro in the area (Boyle, 1965, p. 104). The value for the single sample of pyrite from the lamprophyre is, likewise, close to the meteoritic standard.

Sulfur Isotope Distribution in Sulfide Deposits

Vein sulfides were concentrated for isotopic analyses from large channel samples cut across the veins and lodes at appropriate places. Great care was taken to ensure that the mineral phases for isotopic analyses were pure. Since the sulfates have a sporadic and irregular occurrence in the oxidized

TABLE 3

SULFUR ISOTOPIC COMPOSITION OF ARSENOPYRITE IN DEPOSITS

Laboratory number	Location and description	δS^{34}‰
S850	No. 6 vein, Keno Hill; massive.	- 1.11
S851	Comstock vein, Keno Hill; massive.	- 3.67
S853	Sadie-Friendship mine, Keno Hill; massive.	- 4.67
S852	Dorothy prospect, Keno Hill; needles.	- 6.89
S848	Dublin Gulch; in pyrite-arsenopyrite-gold veins.	0.00
S849	Dublin Gulch; in pyrite-arsenopyrite-gold veins.	+ 1.33
	Average	- 2.50

TABLE 4

SULFUR ISOTOPIC COMPOSITION OF CHALCOPYRITE IN DEPOSITS

Laboratory number	Location and description	δS^{34}‰
S854	Cream prospect, Galena Hill; massive.	- 5.44
S739	Dublin Gulch area; cassiterite lode, massive.	- 1.78
	Average	- 3.61

TABLE 5

SULFUR ISOTOPIC COMPOSITION OF SPHALERITE IN DEPOSITS

Laboratory number	Location and description	δS^{34}‰
S855	Bellekeno mine, Sourdough Hill; massive.	+ 4.44
S857	Sadie-Friendship mine, Keno Hill; massive.	+ 0.67
S858	Onek mine, Keno Hill; massive.	- 0.67
S859	Lucky Queen mine, Keno Hill; massive.	- 1.33
S860	Klondyke-Keno prospect, Keno Hill; massive.	- 2.66
S861	Galkeno mine, Galena Hill; massive.	+ 1.33
S863	Hector-Calumet mine, Galena Hill; 650 foot level.	- 3.56
S862	Hector-Calumet mine, Galena Hill; 775 foot level.	- 3.56
S866	Gambler prospect, Keno Hill; massive.	- 0.44
S856	Ladue Fraction, Keno Hill; massive.	- 0.67
	Average	- 0.64

TABLE 6

SULFUR ISOTOPIC COMPOSITION OF GALENA IN DEPOSITS

Laboratory number	Location and description	δS^{34}‰
Sourdough Hill:		
S947	Bellekeno mine, Sourdough Hill; vein A, crystals.	- 1.56
S946	Bellekeno mine, Sourdough Hill; vein A, massive.	- 0.89
S948	Bellekeno mine, Sourdough Hill; vein A, crystals.	- 1.33
S949	Bellekeno mine, Sourdough Hill; vein A, massive.	- 0.22
S951	Bellekeno mine, Sourdough Hill; vein E, massive.	- 0.22
S955	Bellekeno mine, Sourdough Hill; vein F, massive.	- 1.45
S956	Bellekeno mine, Sourdough Hill; vein F, massive.	- 0.67
S957	Bellekeno mine, Sourdough Hill; vein G, massive.	+ 0.22
S958	Bellekeno mine, Sourdough Hill; vein F, massive.	0.00
S959	Bellekeno mine, Sourdough Hill; vein F, sheared.	0.00
S960	Bellekeno mine, Sourdough Hill; vein F, schistose.	- 1.56
S961	Bellekeno mine, Sourdough Hill; vein F, massive.	- 1.33
S962	Bellekeno mine, Sourdough Hill; vein H, nodular.	+ 0.22
S963	Bellekeno mine, Sourdough Hill; vein F, massive.	- 1.22
S967	Bellekeno mine, Sourdough Hill; vein F, massive.	0.00
S969	Bellekeno mine, Sourdough Hill; vein F, massive.	- 0.89
S964	Bellekeno mine, Sourdough Hill; vein G, massive.	- 1.11
	Average	- 0.71
Keno Hill:		
S970	Mount Keno prospect, Keno Hill; Hogan vei , massive.	- 1.78
S971	Mount Keno prospect, Keno Hill; Runer vein, massive.	+ 0.67
S972	Mount Keno prospect, Keno Hill; Runer vein, massive.	+ 0.22
S973	Mount Keno prospect, Keno Hill; Runer vein, massive.	- 0.89
S974	Onek mine, Keno Hill; Lone Star shaft, massive.	- 3.78
S975	Onek mine, Keno Hill; 400 foot level, massive.	- 3.67
S965	Onek mine, Keno Hill; Fisher shaft, massive.	- 3.78
S976	Lucky Queen mine, Keno Hill; massive.	- 2.67
S977	Lucky Queen mine, Keno Hill; massive.	- 3.33
S979	Klondyke Keno prospect, Keno Hill; E-W vein, massive.	- 5.56
S980	Klondyke Keno prospect, Keno Hill; E-W vein, massive.	- 5.78
S981	Klondyke Keno prospect, Keno Hill; N-S vein, massive.	- 3.44
S982	Klondyke Keno prospect, Keno Hill; N-S vein, massive.	- 3.33
S990	Sadie-Friendship mine, Keno Hill; medium-grained, massive.	- 5.11
S991	Sadie-Friendship mine, Keno Hill; fine-grained, massive.	- 3.78
S992	Sadie-Friendship mine, Keno Hill; medium-grained, massive.	- 2.89
S994	Sadie-Friendship mine, Keno Hill; coarse, massive.	- 4.22
S993	Sadie-Friendship mine, Keno Hill; microcrystalline.	- 3.11
S995	Sadie-Friendship mine, Keno Hill; fine-grained.	- 4.44
Keno Hill (continued):		
S987	No. 9 vein system, Keno Hill; composite.	- 2.00
S1654	Gambler prospect, Keno Hill; massive.	- 4.22
S985	Shamrock vein, Keno Hill; massive.	- 4.11
S986	Shamrock vein extension, Keno Hill; massive.	- 2.67
S984	Comstock prospect, Keno Hill; massive.	- 1.56
S983	Cariboo prospect, Keno Hill; massive.	- 8.67
	Average:	- 3.36
Galena Hill:		
S996	Galkeno mine, Galena Hill; Sugiyama vein, massive.	- 2.44
S997	Galkeno mine, Galena Hill; Sugiyama vein, massive.	- 2.22
S1651	Galkeno mine, Galena Hill; McLeod vein, massive.	- 7.67
S999	Galkeno mine, Galena Hill; McLeod vein, massive.	- 2.89
S1062	Galkeno mine, Galena Hill; McLeod vein, massive.	- 2.33
S1064	Galkeno mine, Galena Hill; McLeod vein, leached galena.	- 4.22
S1000	Dragon claim, Galena Hill; massive.	- 7.11
S1002	Formo prospect, Galena Hill; coarse-grained, massive.	-12.00
S1003	Formo prospect, Galena Hill; fine-grained, massive.	-11.22
S1004	Formo prospect, Galena Hill; microcrystalline.	- 8.67
S1005	Dixie prospect, Galena Hill; massive.	- 8.89
S1009	Arctic and Mastiff prospect, Galena Hill; massive.	- 8.00
S1011	Arctic and Mastiff prospect, Galena Hill; massive.	- 4.44
S1032	Silver King mine, Galena Hill; massive.	- 8.22
S1033	Silver King mine, Galena Hill; gneissic.	- 9.11
S1041	Silver King mine, Galena Hill; massive.	-11.56
S1035	Cream prospect, Galena Hill; massive.	- 8.00
S1036	NoCash mine, Galena Hill; fine-grained, massive.	- 4.44
S1037	NoCash mine, Galena Hill.	- 7.33
S1038	Coral and Wigwam prospect, Galena Hill; massive.	- 3.78
S1039	Elsa mine, Galena Hill; massive.	- 9.22
S1044	Big Horn Creek, Mount Haldane; massive.	- 5.45
S1655	Hector-Calumet mine, surface, Galena Hill; massive.	- 7.78
S1013	Hector-Calumet mine, Galena Hill; 100 foot level, massive.	- 5.56
S1014	Hector-Calumet mine, Galena Hill; 100 foot level, massive.	- 7.11
S1015	Hector-Calumet mine, Galena Hill; 300 foot level, massive.	- 6.44
S1016	Hector-Calumet mine, Galena Hill; 300 foot level, massive.	- 6.50
S1018	Hector-Calumet mine, Galena Hill; 300 foot level, massive.	- 7.11
S1022	Hector-Calumet mine, Galena Hill; 400 foot level, coarse-grained massive.	- 5.33
S1023	Hector-Calumet mine, Galena Hill; 400 foot level, gneissic.	- 6.44
S1024	Hector-Calumet mine, Galena Hill; 400 foot level, massive.	- 5.33
S1025	Hector-Calumet mine, Galena Hill; 400 foot level, gneissic.	- 5.56
S1646	Hector-Calumet mine, Galena Hill; 400 foot level, massive.	- 7.78
S1028	Hector-Calumet mine, Galena Hill; 525 foot level, massive and gneissic.	- 6.67
S1029	Hector-Calumet mine, Galena Hill; 525 foot level, massive.	- 6.44
S1030	Hector-Calumet mine, Galena Hill; 650 foot level, massive.	- 7.78
S1031	Hector-Calumet mine, Galena Hill; 650 foot level, massive.	- 6.81
S1046	Hector-Calumet mine, Galena Hill; 775 foot level, massive.	- 6.00
S1052	Hector-Calumet mine, Galena Hill; 775 foot level, massive.	- 5.56
S1059	Hector-Calumet mine, Galena Hill; 900 foot level, composite sample.	- 3.26
	Average	- 6.57

TABLE 7

SULFUR ISOTOPIC COMPOSITION OF SULFOSALTS IN DEPOSITS

Laboratory number	Location and description	δS^{34} ‰
S989	Boulangerite, Sadie-Friendship mine, Keno Hill.	- 7.11
S1001	Boulangerite, Dragon prospect, Galena Hill.	- 5.56
S870 to S875 S1012	Jamesonite, zinkenite, etc., Dublin Gulch area average of 7 samples.	- 0.65 (± 0.5)
S1640	Freibergite in comb quartz, Klondyke-Keno prospect, Keno Hill	- 5.11
S1639	Freibergite, Sadie-Friendship mine, Keno Hill	- 2.22
S869	Freibergite, Hector-Calumet mine, Galena Hill	- 3.78
S1660	Freibergite, boulangerite, etc. in siderite Sadie-Friendship mine, Keno Hill	- 18.67
	Average (less S1660)	- 4.07

zones grab samples only were obtained for most of the supergene sulfates analyzed.

Hypogene Sulfides and Sulfosalts.—The results of the isotopic analyses of the various sulfides and sulfosalts in the deposits are given in Tables 2 to 7 inclusive, and the ranges and averages are shown in Table 13 and Figure 2. The following points are evident:

The vein pyrite (Table 2) shows considerable variation in its isotopic composition, but most ore shoots contain pyrite depleted in S^{34}, the average of 32 analyses being −2.45‰. There are no apparent major differences between the isotopic composition of pyrite in the early quartz veins (Samples S815, S816, S760, S761) and that in the late siderite lodes.

TABLE 8

SULFUR ISOTOPIC COMPOSITION (δS^{34} ‰) OF COEXISTING SULFIDES IN DEPOSITS

Location	Pyrite	Sphalerite	Galena
Hector-Calumet mine 650 foot level Galena Hill	-2.44 -2.22	-3.56 —	-7.76 -6.84
Hector-Calumet mine 775 foot level Galena Hill	-2.44 -2.67	-3.56 —	-6.00 -5.56

In the Hector-Calumet mine, the largest and most productive in the area, all of the pyrite is depleted in S^{34}, and there is no apparent correlation of the isotopic composition with depth.

The arsenopyrite (Table 3) exhibits a rather restricted range in isotopic composition, most samples in the oreshoots being depleted in S^{34}. There are some significant differences between the isotopic composition of arsenopyrite in the early quartz veins (Samples S850, S851, S848, S849) and that in the late siderite lodes.

Both samples of chalcopyrite (Table 4) are depleted in S^{34}. The sphalerite results (Table 5) define a range from +4.44 to −3.56, the majority of the samples being depleted in S^{34}, with a slightly negative average delta value of −0.64‰.

Galena (Table 6) shows a predominant depletion in S^{34} in nearly all oreshoots, and distinctly different average delta values for the deposits on the three hills. The deposits on Sourdough Hill are the least depleted in S^{34} (−0.71); those on Keno and Galena Hills show progressively greater depletions and possess average delta values of −3.36 and −6.57, respectively (Fig. 2). In the Hector-Calumet mine

TABLE 9

COMPARISON OF SULFUR ISOTOPIC COMPOSITION (δS^{34} ‰) OF SPHALERITE & GALENA IN DEPOSITS

Area	Location	Sample No.	Sphalerite	Galena	$\Delta\ \delta S^{34}$ ‰
Sourdough Hill	Bellekeno mine	S 855 Average of 17 samples, Table 6	+4.44	-0.71	5.2
Keno Hill	Sadie-Friendship mine	S 857 Average of 6 samples, Table 6	+0.67	-3.93	4.6
	Onek mine	S 858 Average of 3 samples, Table 6	-0.67	-3.74	3.1
	Lucky Queen mine	S 859 Average of S 976, S 977, Table 6	-1.33	-3.00	1.7
	Klondyke-Keno prospect	S 860 Average of S 981, S 982, Table 6	-2.66	-3.39	0.7
	Gambler prospect	S 866 S 1654	-0.44	-4.22	3.8
Galena Hill	Galkeno mine	S 861 Average of 6 samples, Table ′	+1.33	-3.63	5.0
	Hector-Calumet mine 650 foot level	S 863 Average of S 1030, S 1031, Table 6	-3.56	-7.30	3.7
	Hector-Calumet mine 775 foot level	S 862 Average of S 1046, S 1052, Table 6	-3.56	-5.78	2.2
				Average difference	3.3

TABLE 10

SULFUR ISOTOPIC COMPOSITION OF HYPOGENE BARITE IN DEPOSITS

Laboratory number	Location and description	$\delta S^{34}‰$
S881	Bellekeno system, Sourdough Hill; crystalline.	+13.78
S901	Bellekeno system, Sourdough Hill; massive crystalline.	+11.44
S879	Porcupine prospect, Keno-Hill; massive crystalline.	+16.67
	Average	+13.96

the delta values are relatively constant over the depth range from 100 to 900 feet, a feature similar to that noted above for pyrite.

All of the sulfosalts listed in Table 7 are depleted in S^{34}, with an average value of −4.07.

The principal feature of the vein sulfides and sulfosalts is that, on the average, all are depleted in S^{34} compared with the pyrite of the country rocks (Table 13 and Fig. 2). In addition there appears to be a progressive depletion in S^{34} with respect to the paragenetic sequence in some vein systems. Thus, the early sulfides including pyrite, arsenopyrite, and sphalerite contain more S^{34} than the later galena, sulfosalts, and chalcopyrite. The reasons for this are not known, but it is interesting to note that this same relationship was first noted at Yellowknife (Wanless, Boyle, and Lowdon, 1961). One explanation could be that the mineralizing medium became progressively depleted in S^{34} as pyrite, arsenopyrite, sphalerite, galena, sulfosalts, and chalcopyrite were sequentially precipitated. Alternatively, atoms of lead and copper may have some specific selectivity for S^{32}, the lighter sulfur isotope. If so, the phenomenon involves complicated bond energies that require experimental examination as Bachinski (1969) has suggested. Whatever the reason, there is growing evidence, such as that shown in Table 8, that pyrite in deposits is richer in S^{34} than coexisting sphalerite, and sphalerite in turn contains more S^{34} than galena.. In the present study we have found that sphalerite consistently contains more S^{34} than galena in eight deposits (Table 9), and while the absolute delta values vary from one deposit to another the difference remains relatively constant with an average $\Delta \delta S^{34}‰$ value of 3.3. This trend has also been noted recently by Stanton and Rafter (1967) and Lusk and Crocket (1969).

Hypogene Sulfates.—The only hypogene sulfate noted in the deposits is barite. It is a late mineral that appears to have crystallized after the sulfides and sulfosalts. The results obtained for three samples (Table 10) indicate extensive enrichment in S^{34} compared with the associated vein sulfides.

Supergene Sulfides and Sulfates.—The only supergene sulfide noted in some quantity in the deposits was galena. Two sulfur isotopic analyses of this sulfide from two places in the Galkeno mine (Table 11) indicate that a significant average shift ($\Delta \delta S^{34} = 7.6$) toward enrichment in S^{32} has occurred during the formation of the supergene galena when compared with hypogene samples of pyrite from which the sulfur was probably derived (Samples S821 and S775, Table 2).

TABLE 11

SULFUR ISOTOPIC COMPOSITION OF SUPERGENE GALENA

Laboratory number	Location and Description	$\delta S^{34}‰$
S1061	Galkeno mine	- 12.78
S1065	Galkeno mine, associated with supergene quartz	- 4.22

The results of the isotopic analyses of the various supergene sulfates in the deposits are given in Table 12 and the range and average are shown in Table 13 and Figure 2. The following points are evident.

The majority of the supergene sulfates are enriched in S^{32} as are the hypogene sulfides and sulfosalts from which they are derived. In some places conversion to sulfate is accompanied by a slight shift in the ratio toward enrichment in S^{34}; in others the

TABLE 12

SULFUR ISOTOPIC COMPOSITION OF SUPERGENE SULFATES

Laboratory number	Location and description	$\delta S^{34}‰$
Sourdough Hill:		
S883	Bellekeno mine, Sourdough Hill; gypsum crystals. (Probably derived from pyrite in S810, S811 and S812.)	+ 0.22
S884	Bellekeno mine, Sourdough Hill; gypsum crystals. (Probably derived from pyrite in S810, S811 and S812.)	+ 0.56
S954	Bellekeno system, Sourdough Hill; anglesite, associated with S951.	- 0.44
S1740	Bellekeno system, Sourdough Hill; anglesite, associated with S960.	- 1.56
S885	Bellekeno mine, Sourdough Hill; anglesite, associated with S967	- 1.11
S968	Bellekeno mine, Sourdough Hill; anglesite encrusting sample S969.	- 0.89
	Average	- 0.54
Keno and Galena Hills:		
S1699	Caribou prospect, Keno Hill; anglesite encrusting sample S983.	- 9.33
S893	Dragon prospect, Galena Hill; anglesite, associated with S1000.	- 4.22
S894	Hector-Calumet mine, Galena Hill; anglesite, associated with S1655.	- 7.11
S897	Hector-Calumet mine, Galena Hill; anglesite encrusting sample S1013.	- 1.56
S1698	No Cash mine, Galena Hill; anglesite, associated with S1037.	- 4.44
S887	Mount Keno prospect, Keno Hill; soluble iron and zinc sulfates, associated with sample S762.	- 4.00
S888	Comstock prospect, Keno Hill; various soluble iron sulfates in seams in oxidized zone.	- 1.77
S1661	Silver King mine, Galena Hill; various soluble iron sulfates (szmikite, ilesite, etc. associated with samples S754 and S755.	- 8.00
	Average	- 5.05
S878	Sulfates in water leaching Hector-Calumet orebodies.	- 2.67

TABLE 13

SUMMARY OF SULFUR ISOTOPIC DATA, KENO HILL-GALENA HILL AREA, YUKON

Description	Table number	Number of samples	Range of δS^{34} ‰	Average of δS^{34} ‰
Pyrite in country rocks				
Graphitic schists and phyllites	1	15	- 5.11 - + 4.44	+ 0.63
Pyritic sericite schist	1	3	- 0.22 - + 6.44	+ 3.48
Quartzites	1	11	- 0.89 - +14.89	+ 2.89
Greenstones	1	7	- 2.44 - + 2.89	+ 0.03
Biotite lamprophyre	1	1	-0.22	- 0.22
Pyrite in deposits	2	33	-21.11 - + 1.56	- 2.45
Arsenopyrite in deposits	3	6	- 6.89 - + 1.33	- 2.50
Sphalerite in deposits	5	10	- 3.56 - + 4.44	- 0.64
Galena in deposits				
Sourdough Hill	6	17	- 1.56 - + 0.22	- 0.71
Keno Hill	6	25	- 8.67 - + 0.67	- 3.36
Galena Hill	6	40	-12.00 - - 2.22	- 6.57
Sulfosalts in deposits	7	7	-18.67 - - 0.65	- 4.07
Chalcopyrite in deposits	4	2	- 5.44 - - 1.78	- 3.61
Barite in deposits	10	3	+11.44 - +16.67	+13.96
Supergene galena	11	2	- 4.22 - -12.78	- 8.50
Supergene sulfates in deposits				
Sourdough Hill	12	6	- 1.56 - + 0.56	- 0.54
Keno and Galena Hills	12	8	- 9.33 - - 1.56	- 5.05
Sulfates in ground waters	12	1	-2.67	- 2.67

reverse is true. This probably reflects local chemical conditions in the oxidized zones; in some places bacterial activity may have been extensive whereas in others such activity was minimal.

The isotopic ratios of the supergene sulfates are in marked contrast to the ratios obtained for the hypogene sulfates (barite), the latter being greatly enriched in S^{34}. In this respect our data corroborate those published recently by Field (1966) and Jensen et al. (1968).

The sulfur isotopic composition of the soluble sulfates in the oxidized zones and the sulfate in the oxidizing waters leaching the hypogene sulfates of the orebodies indicates an enrichment in S^{32}, reflecting the ratio present in the ores. This could provide a valuable geochemical prospecting technique for distinguishing springs which derive their sulfate from hypogene ores compared with those that derive their sulfate from disseminated sulfides in the country rocks.

Discussion and Conclusions

Boyle (1965) has suggested that the Keno Hill-Galena Hill deposits originated as a result of the diffusion of ore and gangue elements from the country rocks into the present vein sites. The isotopic data on sulfur tend to support this contention. Thus, during the diffusion process from the rocks the lighter sulfur isotope, S^{32}, has been selectively concentrated in the vein sites. This feature was also noted at Yellowknife (Wanless, Boyle, and Lowdon, 1961) for those sulfide veins where extensive chemical reaction and wall rock alteration was absent, as it is in the Keno Hill-Galena Hill deposits.

Alternatively one could suggest that the sulfur in the lodes in the Keno Hill-Galena Hill area was derived from a magmatic or other source independent of the country rocks. Since this source is not identifiable the diffusion hypothesis of sulfur from the country rocks is preferred.

The marked differences in the sulfur isotope distribution in minerals such as galena in the deposits of the three hills in the area—Sourdough, Keno, and Galena—appear to us to be real, although the reasons for the differences are obscure. If the sulfur was derived from a single magmatic or other deep homogeneous source such differences are difficult to explain. On the other hand, if a source in the sediments is assumed, inhomogeneities in the source beds, as shown by our analyses, would be expected to produce sulfide bodies with differing isotopic ratios such as we have found.

Finally, it seems probable that sulfur isotopic analyses can be used as a geochemical prospecting technique in hydrogeochemical surveys to distinguish circulating waters that leach sulfur (sulfate) from mineralized zones from those that derive the element from barren rocks. More research along this line is projected in our laboratories.

GEOLOGICAL SURVEY OF CANADA,
OTTAWA, CANADA,
June 29, 1969

REFERENCES

Bachinski, D. J., 1969, Bond strength and sulfur isotopic fractionation in coexisting sulfides: ECON. GEOL., v. 64, pp. 56–65.

Boyle, R. W., 1965, Geology, geochemistry, and origin of the lead-zinc-silver deposits of the Keno Hill-Galena Hill area, Yukon Territory: Geol. Surv. Canada, Bull. 111

Carmichael, A. D., 1957, United Keno Hill mines: Structural Geology of Canadian Ore Deposits, v. 2, pp. 66–67.

Field, C. W., 1966, Sulfur isotopic method for discriminating between sulfates of hypogene and supergene origin: ECON. GEOL., v. 61, pp. 1428–1435.

Green, L. H., and Roddick, J. A., 1962, Dawson, Larsen Creek, and Nash Creek Map-areas, Yukon Territory: Geol. Surv. Can., Paper 62-7.

Jensen, M. L., Mauger, R. L., Albers, J., and Ashley, R. P., 1968, Primary and secondary sulfates as ore guides at Goldfield, Nevada: *in* Annual Report, Laboratory of Isotope Geology, Department of Geological and Geophysical Sciences, University of Utah, Salt Lake City, Utah, pp. 56–64.

Lusk, J., and Crocket, J. H., 1969, Sulfur isotope fractionation in coexisting sulfides from the Heath Steele B-1 orebody, New Brunswick, Canada: ECON. GEOL., v. 64, pp. 147–155.

McTaggart, K. C., 1960, The geology of Keno and Galena Hills, Yukon Territory: Geol. Surv. Canada, Bull. 58.

Stanton, R. L., and Rafter, T. A., 1967, Sulfur isotope ratios in coexisting galena and sphalerite from Broken Hill, New South Wales: ECON. GEOL., v. 62, pp. 1088–1091.

Wanless, R. K., Boyle, R. W., and Lowdon, J. A., 1961, Sulfur isotope investigation of the gold-quartz deposits of the Yellowknife district: ECON. GEOL., v. 55, pp. 1591–1621.

Wanless, R. K., Stevens, R. D., Lachance, G. R., and Edmonds, C. M., 1967, Age determinations and geological studies; K-Ar isotopic ages, Report 7: Geol. Surv. Canada, Paper 66–17.