CHAPTER 1

INTRODUCTION

Nature and Purpose of Report

The barite-celestite-fluorite project was
initiated in 1974 because of the increasingly important
role these minerals are playing in the maintanence and
development of technologically advanced countries
throughout the world. It was the intention of this
project to provide interested parties with all the
pertinent, up to date data on each barite, celestite and
fluorite deposit in the province and to stimulate groups
who are exploring and developing such mineral deposits
to recognize Nova Scotia as an area with a high potential
for these resources. It was also hoped that this study
would reveal geological associations which would indicate
favourable sites for investigation hitherto unexplored for
barite, celestite and fluorite.

Barite, Celestite and Fluorite: Uses, Specifications, Potential, and Prices*

Barite

The greatest portion (approximately 80%) of the
world barite production is consumed in the oil and gas
exploration industry. The remainder is used by various
other industries, most notably glass, chemical and rubber
manufacturers, in a host of products. One of the newest
uses for barite, although consumption is still rather
limited, is its addition to concrete aggregate in the
construction of atomic reactors. This new application of
barite is a result of its ability to absorb gamma radiation.

In the oil and gas exploration industry barite
finds its use in drilling mud for which it is particularly
well suited. Barite is soft (consequently easily crushed and
non-abrasive), virtually chemically inert, and has a high
specific gravity. These features are important in drilling
mud, which must have a sufficiently high specific gravity

* A more complete and more detailed breakdown of this topic
  can be found in the literature, some of the more recent
  of which are listed in the bibliography at the end of
  this report.

to contain downhole pressures, must be relatively non-abrasive to prevent excessive wear on the drill stems and sufficiently chemically inert to be totally non-reactive with substances encountered during drilling. Specifications generally required by the oil and gas industry for barite are that it have a specific gravity of no less than 4.2 (approximately 93 per cent $BaSO_4$), a soluble salt content of <0.1 per cent, an iron oxide content not exceeding several per cent, and that it be ground to minus 325 mesh.

In the manufacture of glass, the addition of barite homogenizes the melt and is found to give glass a greater clarity and brilliance. Specifications for barite vary with each individual glassmaker; however, in general, it must be about 97 per cent $BaSO_4$ with a maximum Fe_2O_3 content of 0.1 to 0.2 per cent and only a trace of TiO_2. Sizing specifications are also variable, although the maximum and minimum are generally 16 and 100 mesh respectively.

The chemical industry generally specifies barite containing 95 per cent $BaSO_4$ with impurities restricted to <1 per cent iron oxide, 1 per cent strontium sulphate, and only traces of fluorine. Size specifications, for the most part, range between 4 and 20 mesh.

The use of barium in the chemical industry is highly diverse. Brobst (1973, p. 76) indicates that barium, in various chemical forms, has over 2,000 specific industrial applications.

In the rubber industry, where barite is used as a filler, a raw material that will pass a 325 mesh is required, and often it must possess a high degree of whiteness.

The world consumption of barite is increasing primarily as a result of increased activity in the oil and gas exploration industry. With world energy requirements growing ever larger, a high level of demand for barite is insured for quite some time. A brisk market for pharma-ceutical barite has prompted a business consortium to undertake a feasibility study of the barite deposit at Upper Brookfield, Nova Scotia. In addition, technological advances are certain to continue to find new uses for barite, thereby contributing to a market expansion.

Current prices for barite vary according to the

specification requirements met by the ore; however they generally range between $30 a short ton and $60 a short ton. Up to date prices are quoted monthly in the Engineering and Mining Journal.

Celestite

Celestite is the principal source of strontium used by industry. Approximately 95 per cent of the world's production is consumed by the chemical industry for conversion to various strontium compounds, the most important of which are strontium carbonate and strontium nitrate. The remaining 5 per cent is used by the producers of electrolytic zinc. Strontium carbonate finds its primary use in the manufacturing of glass face plates for colour televisions, where it filters out harmful radiation. A less important although steadily growing use for strontium carbonate, is in the production of ferrites for permanent magnets. Strontium nitrate is used principally in the pyrotechnic industry for the manufacturing of safety flares. Strontium nitrate is particularly well suited to this use because of the bright, crimson red flame that is emitted upon oxidation. Other products containing strontium compounds include greases, alloys, anticorrosive paints, ceramics, and pharmaceuticals.

Quality specifications for celestite used in the production of strontium carbonate are: a minimum content of 90 per cent $SrSO_4$, and a maximum content of 2 per cent $BaSO_4$, and 0.1 per cent fluorine. For the manufacture of strontium nitrate, the minimum $SrSO_4$ content is 95 per cent, and the maximum allowable amounts of $CaSO_4$ and $BaSO_4$ are 1.5 and 2 per cent respectively.

Markets for celestite are increasing slowly but steadily chiefly due to the increasing consumption of $SrCO_3$ in the manufacturing of ferrites. Unfortunately, the demand for strontium ferrites has not grown as rapidly as was expected. Consequently, the current market situation and future potential for celestite is not as favourable as that for barite. This rather weak market resulted in the 1976 closing of North America's (excluding Mexico) only celestite mine, at Loch Lomond, Nova Scotia. A substantial expansion of the celestite market in the future would greatly enhance the profitability of celestite mining. Technological advances resulting in new uses for strontium will play a significant role in bringing about this market expansion.

Prices for celestite with a $SrSO_4$ content of approximately 92-93 per cent range from $20 a short ton to $38 a short ton. Technical grade $SrCO_3$ commands between $.18 and $.25 a pound, and $Sr(NO_3)$, generally brings $24 per 100 pounds. Current up to date prices are quoted in the Chemical Marketing Reporter.

Fluorite

The three major consumers of fluorite are: (a) the chemical industry, where fluorite is converted to other fluorine bearing compounds which in turn have numerous applications, (b) the ceramics industry, and (c) the iron and steel industry.

In the chemical industry, the majority of the fluorite is consumed in the production of HF. The principal uses for HF include, (a) the manufacture of cryolite required in the aluminum making industry, (b) glass etching and polishing, (c) as a catalyst in the production of high octane fuels, (d) steel pickling, and (e) the manufacturing of organic fluorides which in turn also have a host of uses including refrigerants, aerosol propellants, fluorocarbon resins etc. Indirectly, the production of one ton of virgin aluminum requires up to 120 pounds of fluorite.

Large quantities of fluorite are consumed by ceramics producers (up to 200 pounds of fluorite per 1000 pounds of sand) in the production of opal glasses. Opal glasses find uses in the container industry for cosmetics and food, the production of ornamental glassware and lavatory fixtures. The opaque enamels coating refriger-ators, stoves, bathtubs etc., contain quantities of fluorite ranging from 3 to 10 per cent by weight.

The steel industry uses fluorite at the rate of 2-20 pounds per ton of steel produced. In the basic oxygen open hearth and electric furnaces, fluorite is required to promote fluidity of the slag which facilitates the expulsion of phosphorus and sulfur from the steel. Iron foundaries consume fluorite in quantities ranging from 15 to 20 pounds per ton of iron melted.

The three major consumers of fluorite specify different grades required for their particular industry. These are: (a) acid grade for the chemicals industry, (b)

ceramic grade for the ceramics industry, and (c) metal-
lurgical grade for the iron and steel industry. Acid
grade must contain a minimum of 97 per cent CaF_2, a maximum
of 1.0 to 1.5 per cent silica and no more than 0.03 to
0.10 per cent sulphur. Ceramic grade is actually broken
down into two grades: No. 1 ceramic and No. 2 ceramic,
with the former having the more rigid specification
requirements. Ceramic No. 1 must contain 95 to 96 per
cent CaF_2 while ceramic No. 2 may contain CaF_2 in amounts
ranging from 85 to over 90 per cent. Impurity restrictions
include maximum quantities of silica ranging from 2.5 to 3
per cent, limited amounts of calcite and a maximum of 0.12
per cent ferric oxide. Restrictions vary according to the
individual user's requirements.

Metallurgical grade fluorite is the poorest
quality fluorite sold on the market; the "effective" CaF_2
per cent sometimes being as low as 60 ("effective" % CaF_2 =
% CaF_2 - % silica x 2.5). Fluorite used for metallurgical
purposes is often referred to as "metspar."

The demand for fluorite has increased steadily
in the past 20 years, resulting in higher prices and
renewed exploration activity. Despite the fact that
advanced technology is reducing the quantities of fluorite
required to make a ton of steel and aluminum (the major
consumers of fluorite), the expanding requirement for
these products as the world continues to industrialize is
certain to insure a brisk market. In addition, the
diversity of uses for fluorite, particularly in the field
of fluorocarbons, should continue to expand resulting in a
continued stable market future for this mineral.

Prices for fluorite vary according to grade, the
distances from the f.o.b. shipping point to the market
areas, and method of shipment (i.e. bagged or bulk). U.S.
fluorspar price ranges for acid, ceramic and metallurgical
grades are $95-$125, $90-$115, and $83-$88 a ton. Up to
date quotes on fluorspar prices are available in the
Engineering and Mining Journal.

Review of Production and Consumption of Barite, Celestite and Fluorite

Relevant statistics pertaining to production and
consumption are graphically illustrated in Figures 1, 2,
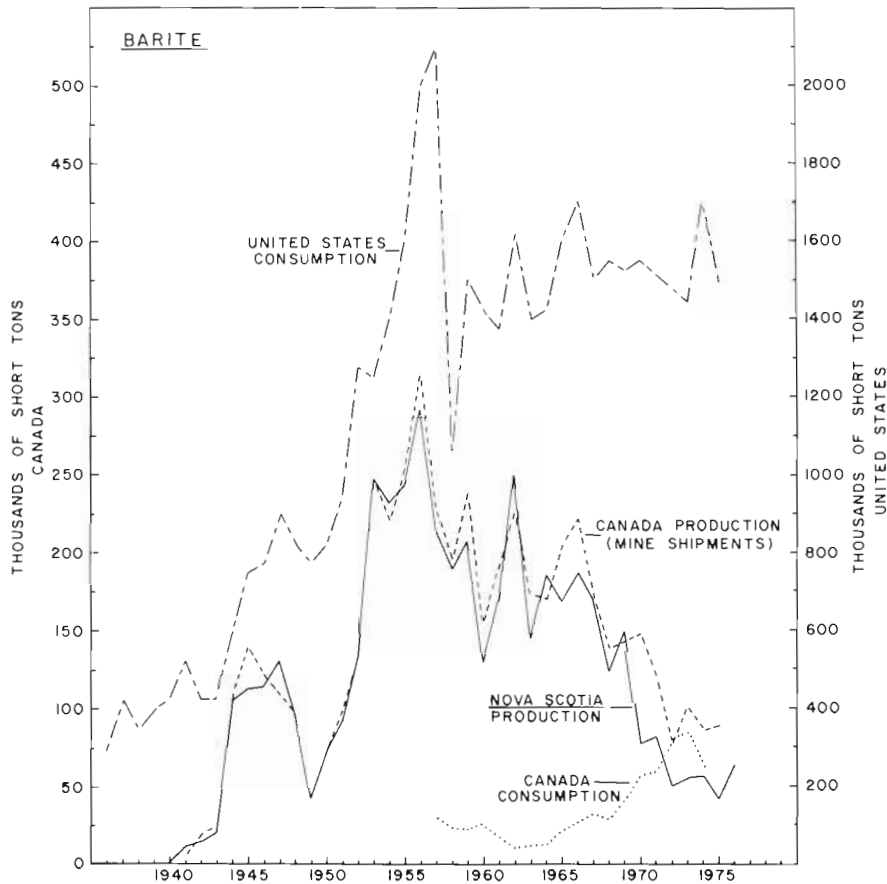and 3. Sources for the statistics include the Canadian

Figure 1 - Production (Nova Scotia and Canada) and consumption
(Canada and United States) of barite during the
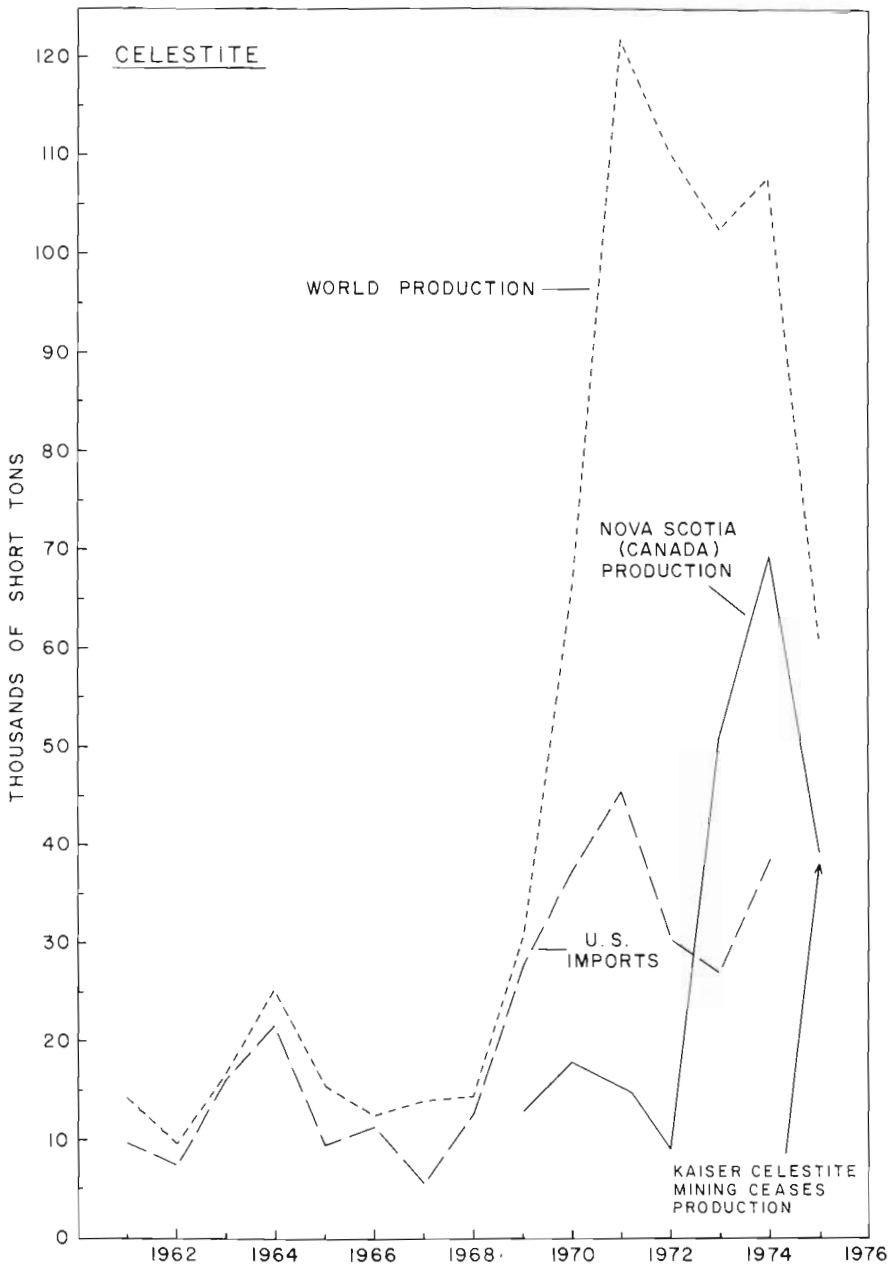period between 1936 and 1976.

Figure 2 - Production (Nova Scotia and World) and imports by
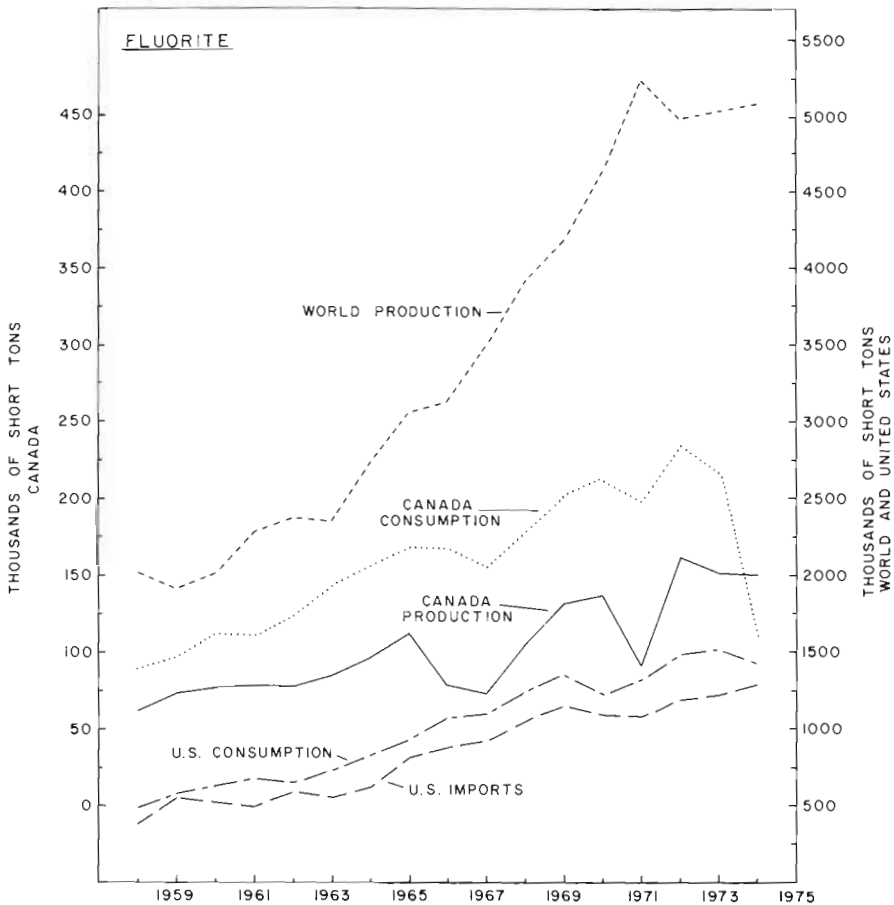the United States of celestite during the period
between 1961 and 1975.

Figure 3 - Production (Canada and World), consumption (Canada and United States), and imports by the United States of fluorite during the period between 1958 and 1974.

Minerals Yearbooks, the U. S. Minerals Yearbooks and the
Nova Scotia Department of Mines Annual Reports.

Terminology

The following list of geological terms are
defined according to the context with which they are used
throughout the report:

paragenesis – the sequential order of mineral formation as
determined from mineral relationships observed
in the field and in a limited amount of thin
section study.

epigenetic – a mineral deposit formed later than the host
rock.

syngenetic – a mineral deposit formed contemporaneously
with the host rock. Mineralization that
could be considered diagenetic, is included
in this definition.

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FIELD INVESTIGATIONS

Previous Work

Previous work by the Department of Mines in this area of industrial minerals is limited, consisting primarily of examination of a number of occurences on Cape Breton Island as part of the Cape Breton Mineral Resources Project (MacNabb, 1973) and Margaree Valley Project (Jones, 1969). Prior to this, two pamphlets on barite, both by Messervey, were published by the Nova Scotia Department of Mines in 1930 and 1950. No studies dealing specifically with celestite or fluorite have been published to date.

Two publications dealing specifically with barite mineralization within restricted areas were published by the Geological Survey of Canada (Poole, 1907; Spence, 1972).

The celestite deposit at Loch Lomond and the barite-fluorite mineralization at Lake Ainslie are the subject of two M.Sc. theses; the former is the topic of a thesis by Choo (Dalhousie University, 1972), and the latter a thesis by Creed (Dalhousie University, 1968). The Loch Lomond and Lake Ainslie deposits are also the subject of papers published by Crowell (1971) and Zurowski (1972) respectively. The Walton barite mine is the subject of an M.Sc. thesis by Shea (1958) and a bulletin by Boyle (1972).

A large number of the showings have been investigated by prospectors and corporations, and their reports comprise the Nova Scotia Department of Mines assessment files.

Present Work

This project aimed to fulfill the following objectives:

(1)   Accurately locate all known occurrences.

(2)   Provide a concise history of exploration on all the occurrences, indicating the types of activities undertaken and the results obtained.   (This information was compiled from data gathered through library research in the Nova Scotia Department of Mines technical services library.)

(3)   Obtain all relevant geological information on each showing.   This includes; (a) descriptions of the host rock, (b) the country rock (where it differs from the host rock), (c) the mineralogy of the deposit, (d) the control of the mineralization (i.e. stratigraphic and/or structural), (e) the presence of wall rock alterations that could be attributed to the mineralization, (f) the presence of features indicating epigenetic or syngenetic origin, and (g) any gross geological features evident in the region surrounding the occurrence (i.e. faulting, folding, igneous intrusions, metamorphism, unconformities, and geological contacts).

The field program was designed to obtain this information in the shortest possible time, consequently the amount of time devoted to detail was short.   It was not within the scope of this project to undertake a metallogenic study of barite, celestite and fluorite, nonetheless, ideas and speculations regarding this topic are presented. The formulation of these thoughts are a result of the study of the available literature (particularly that pertaining to barite, celestite and fluorite mineralization in Nova Scotia), geological evidence obtained through field work, chemical analysis of rock specimens collected in the field, and a limited amount of thin section study.

Procedures in the field included:

(1)   Locating occurrences on 1:50,000 topographic maps;

(2)   Compilation of location and geology maps on a scale as suited for each particular showing. Mapping was carried out by the compass and pace method, plane tableing, air photo interpretation and modification of plans previously constructed by various individuals in the exploration industry.

(3)   Collecting geological data as outlined above.

(4)   Obtaining samples of the mineralized rock, wall rock and in some cases the country rock. These consisted mainly of grab samples though channel samples were collected at a few of the showings.

DETERMINATION OF BARITE, CELESTITE AND FLUORITE

Chemical Methods

All samples were chemically analysed for Cu, Pb, Zn, F, Ba, Sr, Si, Fe, Mn, Al, Ca, and L.O.I. at the Canadian Laboratory for Investigation of Minerals, Nova Scotia Technical College, Halifax, Nova Scotia. The methods employed for each of these elements are listed below:

    Atomic absorption - Cu, Pb, Zn, Ca, Sr >1.0%, Fe,
                         Al, Mn, Si
    Gravimetric   - Ba >1.0%, Si, L.O.I.
    Volumetric   - F
    Spectrographic   - Ba <1.0%, Sr >1.0%

Mineralogic Methods

The presence of barite and celestite in hand specimens was determined primarily by the following physical properties; (a) high specific gravity, (b) crystal structure (orthorhombic), and (c) lack of effervescence in dilute HCl. It is very difficult to distinguish barite from celestite without resorting to a flame test, micro-scopic examination or chemical analysis. Optically, barite and celestite are very similar, however a distinctive feature is the 2V angle which is larger in celestite than barite.

Physical properties which reveal the presence of fluorite in hand specimens include; (a) hardness (4), (b) crystal structure (isometric), (c) relative insolubility in dilute HCl. Optical properties characteristic of fluorite are it's high relief, isotropic character and perfect octahedral cleavage.

GENERAL REVIEW OF MINERALOGIC CHARACTERISTICS OF BARITE, CELESTITE AND FLUORITE

Barite is a member of the sulfate series of minerals with the chemical formula $BaSO_4$. The crystallographic structure of barite is orthorhombic dipyramidal, which is expressed in a variety of habits. When found well crystallized, the most common habit is thin to thick tabular aggregates of crystals projecting into crest like forms. Generally, barite occurs in a massive form varying in grain size from cryptocrystalline to very coarse grained.

It is a brittle mineral, has a hardness ranging from 3 to 3.5 on the Mohs scale, and a specific gravity of 4.5. Cleavage is perfect along (001) and very good along (210), thus when occurring in a very coarsely crystalline state, it will part readily to form plates up to 4 inches in length and 0.5 inch in thickness. The colour of barite is highly variable; transparent to translucent in well crystallized forms, and red, pink, grey, green, yellow, cream, brown, black and blue in the massive varieties. Most of these colours are due to impurities such as iron oxides, graphite and carbonaceous material within the barite.

When subjected to the flame test, barite produces a green flame.

Like barite, celestite is also part of the sulphate group of minerals with the chemical formula $SrSO_4$. Chemically the two elements barium and strontium are very similar, consequently barite and celestite share many of the same physical properties. Crystallographically, celestite belongs to the orthorhombic system, dipyramidal class, which is expressed in a number of different habits similar to those of barite. The most common is thin to thick, tabular and elongated form. Generally, celestite is found in a fine to coarse-grained, massive form, and often with a granular texture. Fibrous varieties are commonly associated with evaporites.

Celestite is brittle, has an uneven fracture and a hardness ranging from 3 to 3.5 on the Mohs hardness scale. Like barite, it has perfect cleavage along (001) and good cleavage along (210), therefore very coarsely crystalline varieties will often separate into plates much like that described above for barite. The specific gravity of pure celestite is slightly less than barite (3.97+0.01). Celestite is found in a variety of colours, ranging from transparent to white, blue, red, brown, green, grey, and translucent. White, grey and blue are the colours in which it is most often found, the pale celestial blue variety giving the mineral its name. The various colours are generally due to impurities, however the blue is believed to be produced by irradiation.

When subjected to the flame test, celestite emits a crimson flame.

Fluorite is a member of the halide group of minerals, with the chemical formula CaF_2, and crystallographically is part of the hexoctahedral class of the cubic system. Well formed crystals of fluorite are most commonly found exhibiting the cubic habit, and less commonly the octahedral habit. Twinning in fluorite generally occurs as interpenetrating cubes. The perfect octahedral cleavage inherent to fluorite is an important distinguishing feature, as is its hardness of 4 on the Mohs scale. It occurs in a variety of colours: blue, green, purple, amber, white, grey, brown, black and transparent. These colourations are apparently due to one or a combination of the following (Deer, Howie and Zussman, 1966):

(1) Physical disturbance in the crystal structure.

(2) Radioactivity emanating from radioactive inclusions or nearby radioactive material.

(3) Trace amounts of rare earth elements in the crystal structure.

(4) Presence of hydrocarbons.

The textures associated with fluorite when occurring in a massive form vary from cryptocrystalline to very coarsely crystalline. The medium-grained variety often shows a granular texture. The term "fluorescence" was derived from fluorite, as this mineral strongly displays this effect when exposed to ultraviolet light.

GENERAL REVIEW OF GEOCHEMICAL CHARACTERISTICS OF
BARIUM, STRONTIUM AND FLUORINE

Barium and strontium do not occur in sufficient
quantities in the lithosphere to be considered important
as rock forming minerals. The average amounts of barium
and strontium in crustal rocks are 425 ppm and 375 ppm
respectively (Levinson, 1972). Albeit that a significant
portion of Ba and Sr is contributed by the hydrothermal
stage of plutonism and volcanic exhalations, the major
source of these elements to the exogenic cycle is the
weathering of igneous rocks. Barium and strontium are
generally present as trace elements in the rock forming
minerals of igneous rocks, the abundance being determined
by the chemical makeup of the rock. The higher the Ca and
K content of the rock, the higher the content of Sr and
Ba respectively. The close association among these
elements is a result of the similarity in valency and
ionic size, which renders them the characteristic of being
diadochic. The ionic radii, valency and ionic potential
for these elements are listed in Table 1 (Berry & Mason,
1959):

Table 1

Ion	Ionic potential	Ionic radius in $\overset{o}{A}$
Ca^{2+}	2.01	0.99
Sr^{2+}	1.79	1.12
K^{+}	.75	1.33
Ba^{2+}	1.49	1.34

The greater the differences in atomic radius
between two ions the less likely they are to substitute
for each other. Thus, while Sr readily substitutes for Ca
and K, Ba only substitutes for K. In igneous rocks Ca and
K are predominantly contained within the plagioclase and
potash feldspars, and to a lesser extent K is incorporated
within muscovite and biotite. Thus, these are the minerals
that contain the anomalous quantities of Ba and Sr within
their atomic structure. However, due to the smaller ionic
radius of Sr, this element becomes concentrated within the
Ca-bearing minerals which begin to form prior to the
crystalization of potash feldspars in granitic melts.
Therefore, the potash feldspars are almost always highly
enriched in Ba relative to Sr. Investigations have shown
that in igneous rocks, those with compositions in the

intermediate to acid range are the richest in barium and strontium. Data presented by Rankama and Sahama, (1950), indicate that granites generally carry barium and strontium in quantities ranging from 630-1600 ppm and 90-250 ppm respectively; syenites, 620-1600 ppm and approximately 600 ppm respectively; and basic, ultra basic and mafic, 3-60 ppm and 9-170 ppm respectively. It is evident from this data that granites and syenites, and their volcanic equivalents are potentially excellent sources of barium and strontium for sedimentary basins whose provenance can be traced to such rocks. However, this does not necessarily imply that sedimentary rocks derived from these rock types will be anomalously high in barium and strontium. Whether or not these elements will migrate to a more favourable geological setting is dependent upon the physico-chemical conditions in the sedimentary basin.

Barium and strontium released from their host minerals through chemical weathering are mobilized and are capable of migrating as bicarbonate, chloride and sulfate complexes. Once transported to the sea, the behavior of the barium and strontium ions is a function of a number of variables, including the salinity, Eh, pH, and temperature of the waters in the receiving basin. The behavior of Ba and Sr ions in a hypersaline, restricted, evaporating basin will be radically different from that in an ocean under conditions such as are prevalent off the Nova Scotia coast at the present time. However, taking into consideration seawater with a temperature range of between 20°-30° C, and the normal ranges of salinity, Eh and pH associated with such temperatures, it has been found that seawater is always impoverished in barium relative to strontium. The maximum content of barium and strontium in such seawater is 0.05 ppm and 10-15 ppm respectively (Boyle, 1972). The significant difference is partially due to the difference in solubility of barite and celestite in fresh water, which at 20° C is .0022 g/l (2.2 ppm) and .114 g/l (114 ppm) respectively (Boyle, 1972)[*]. This in itself would result in a greater abundance of strontium versus barium supplied in solution to the sea, given a source area with relatively equal quantities of both elements.

Another factor which contributes to the low Ba/Sr ratio in seawater is the adsorption affects of the clay minerals suspended in solution and contained within

* Dana (1951) reports similar solubilities for barite and celestite; .0024 g/l and .132 g/l respectively.

the sediments. Clay minerals, i.e. the hydrolyzates,
strongly adsorb available cations (Ba^{++}, Sr^{++}) to their
surfaces as well as undergo base exchange with these
cations. The base exchange that most readily occurs is
between the K^{+} ions of the hydrolzate and the Ba^{++} ions.
This preference exhibited by clay minerals for Ba over Sr
is attributed to the lower ionic potential and greater
ionic radius of the former as compared with the latter.
This adsorption property of clay minerals (montmorillonite
and illite in particular) results in a low rate of transfer
of barium from that supplied to the sea and that taken up
by seawater. According to data presented by Rankama and
Sahama (1950), the transfer percentage of barium and
strontium is 0.03 and 7.2 respectively. This represents a
Sr/Ba transfer percentage ratio of 240:1, which is consistent
with the average ratio of Sr/Ba generally found in seawater
(approximately 250:1).

        Despite the fact that seawater is normally
impoverished in Ba relative to Sr, and that near the
surface it is generally undersaturated with respect to
both of these elements, Zimmerman (1965) shows the barium
content to increase by a factor of 5 at depth (approx.
5000 M). Barite concretions have been dredged from the
ocean floor at depths of only 2700 feet (Revelle & Emery,
1951). Geologically, the syngenetic deposition of barite
and celestite in shallow and deep water environments is
indicated in a number of deposits in North America, e.g.
Battle Mountain, Nevada; Stevens County, Washington State
(Dawson, 1976); Tom & Moose Properties, Yukon Territory;
Sulphur and 110 Creek Properties, British Columbia (Dawson,
1975); various localities in West-Central Arkansas,
and in the Moreno Shale, California (Zimmerman, 1965).
This suggests that anomalous concentrations of barium and
strontium can occur in marine or lacustrine depositional
environments and that their precipitation as barite and
celestite takes place when favourable physico-chemical
conditions exists.

        The close link that exists between Sr^{++} ions and
Ca^{++} ions in igneous rocks is paralleled by their relatively
close association in sedimentary rocks. However, of the
Ca minerals formed during the exogenic cycle, only those
with a favourable crystal lattice structure commonly
substitute Ca with Sr. The most important of these are
aragonite and anhydrite which crystallize in the ortho-
rhombic system and dipyramidal class and can contain
quantities of strontium ranging as high as several per

cent. In addition to Sr^{++} ions occupying lattice sites normally occupied by Ca^{++} ions, it occupies interstices in the crystal latice and also occurs as inclusions (Bathurst, 1975). The inclusions would either be in fluid or solid (mineral) form. Aragonite expels the Sr contained within its crystal lattice when it converts to its more stable form, calcite, which is capable of incorporating significantly less quantities of Sr within its structure. The Sr that is released is most commonly precipitated as $SrSO_4$, depending upon the availability of SO_4^- ions. Similarly, Sr is exsolved from the anhydrite crystal lattice when that mineral is hydrated to gypsum. This exsolved Sr is expelled into an environment saturated with SO_4^- ions, consequently it is immediately precipitated as $SrSO_4$. It is often difficult to distinguish $SrSO_4$ formed in this manner from syngenetic $SrSO_4$, which is also a common constituent in gypsum.

Thus in the exogenic cycle, hydrolyzates, aragonite, and anhydrite are good 'holding' minerals for barium and strontium, which can later be mobilized and migrate in response to favourable physico-chemical conditions. The physico-chemical conditions which promote the mobilization and migration of these ions are often met with during and after diagenesis, and can result in extensive deposits of barite and celestite. The strong association of celestite deposits with limestones derived from the alteration of aragonite to calcite, and gypsum and anhydrite, is well documented. The source of the Sr for the extensive celestite deposits in the area northeast of Bristol, England is wholly attributed to the Carboniferous Limestone in this area which was originally composed of aragonite (Nickless et al., 1976). The celestite deposits of Loch Lomond, Nova Scotia are in part considered to be a result of Sr derived from anhydrite-gypsum beds (S. Forgeron, 1977). These deposits illustrate the significance of aragonite and anhydrite as a prolific source of abundant Sr.

In summary, exogenically derived Sr and Ba is a major source of these elements, which, depending on the receiving environment, become concentrated in: (a) the K^+ bearing hydrolyzates, (b) the precipitates and evaporates (i.e. aragonite and anhydrite in particular), (c) in seawater and subsequently formational waters (connate waters), and (d) in syngenetic barite and celestite deposits.

Where physical weathering is predominant, and

sedimentation is rapid the major portion of Ba and Sr will remain locked up in the clasts and matrix to be released at a later time through metamorphic processes, ion exchange or leaching. The alteration of feldspars to sericite, and muscovite and biotite to chlorite, as a result of leaching and/or ion exchange is an effective process of mobilization of Ba and Sr. According to Creed (1972), the enrichment of formational waters in Ba and Sr through leaching is of sufficient magnitude in some instances to reduce the required volume of ore-bearing solution for a given ore body by a factor of 10. This appears to be substantiated in studies undertaken by Kozin (1964 in Davidson, 1966, p. 218). Kozin's studies of 460 samples of sandstones from the Russian platform indicate that red-bed formations are ten times more abundant in Ba (averaging 0.38 per cent Ba) than the other types of sandstone represented in the platform. Leaching of such a rock unit would supply significant quantities of Ba to formational waters or brines.

Barite and celestite deposits derived from endogenic sources of Ba and Sr are also common. The source of the essential ions would either be hydrothermal solutions of magmatic origin or volcanic exhalations. In some cases endogenic solutions combine with connate waters, each contributing components that may be absent in the other, but are essential in bringing about the precipitation of ore minerals.

Studies of numerous barite and celestite deposits throughout the world have shown that the two minerals almost always occur together. However, it has been found that one is always highly dominant over the other, with the minor one generally never accounting for more than a few per cent of the mineralization. The reason for this may be that the precipitation of $SrSO_4$ in solution is not temperature dependent in a system characterized by decreasing temperature (Choo, 1972). Since the reverse is true for the precipitation of $BaSO_4$, it would be unlikely for barite and celestite to occur together where decreasing temperature was a major factor in bringing about the precipitation of the mineral phases. In most cases the diadochic character of Ba and Sr probably accounts for the presence of minor quantities of one, where the other predominates.

It is in part because of chemical and mineralogic similarities that barite and celestite have been treated together in the above discussion. Fluorite, on the other

hand, is treated separately because although it is commonly associated with barite, its differing physical and chemical characteristics dictate a somewhat different behaviour in the chemical environment.

Like barium and strontium, fluorine does not occur in sufficient quantities in the lithosphere to be important as a rock forming mineral. However, it is abundant enough [average abundance 625 ppm in crustal rocks (Levinson, 1972)] that it occurs as accessory minerals, fluorite, cryolite and fluorapatite, as well as a trace element in various igneous rock types.

Fluorine belongs to the halogen group of elements, consequently it shows characteristics peculiar to the whole group. Fluorine is strongly lithophile, occurring as a univalent anion with a radius of 1.36 A. Fluorine is unique in that it is the most electronegative of all the elements, and therefore is an extremely good oxidizing agent. Because of this property, fluorine is rarely encountered in an uncombined state. Since the ionic radius of fluorine is identical to that of the OH^- ion and nearly identical to the O^{2-} ion, it will substitute for these ions whenever possible. Consequently, in igneous rocks, fluorine is often encountered, and is most abundant in OH^- bearing silicate minerals such as the micas, amphiboles, tourmaline, and a few other minor accessory minerals. Biotite is capable of containing up to 4.3 per cent F (Rankama and Sahama, 1950), and apatite normally contains about 3.5 per cent F (Smith, 1963). These minerals are most abundant in igneous rocks of intermediate to acid composition, thus these rocks are a good source of F for the exogenic cycle. However, because greater quantities of fluorine become concentrated in the later stages of magmatism than are taken up in minerals formed in the earlier stages, the minerals of fluorine such as fluorite and cryolite in particular are also an important source of this element to the exogenic cycle. Fluorine mobilized through the chemical weathering of micas, amphiboles and tourmaline, will complex with available anions, migrate and precipitate as fluorite under favourable physico-chemical conditions.

Fluorite is relatively insoluable in water, with the natural rivers and lakes containing less than 1 ppm fluorine. However, it is much more soluble in sea water and lacustrine brines, which are reported to contain up to approximately 12 ppm (Creed, 1968) and 1627 ppm fluorine

(Worl et al., 1973) respectively. Natural waters and
seawater are generally undersaturated in fluorine, which
is in part a result of the adsorption property of the
hydrolyzates. The clay minerals, bentonite in particular,
strongly adsorb F⁻ ions to their surfaces. Rankama and
Sahama (1950) report that bentonite can contain up to 7400
ppm fluorine. When groundwater or seawater becomes
saturated or nearly saturated in fluorine, the fossil
fauna contained within the sediments that are exposed to
these waters concentrate significant amounts of this
element in the calcareous remains of their anatomy (i.e.
marine shells, teeth and bones). Microsaur teeth from the
Pennsylvanian rocks of Joggins, Nova Scotia, are found to
contain up to 3.1 per cent fluorine in the form of
fluorapatite (Stevenson and Stevenson, 1966). Such a
concentration could only come about by enrichment as a
result of exposure to fluoride rich waters. Marine
phosphate deposits also contain significant quantities of
fluorine (3 per cent, Worl et al., 1973).

Despite the large contribution of exogenically
derived fluorine to the lithosphere an even greater amount
is contributed by volcanic emanations. Data indicate that
volcanic emanations can contain up to 149,000 ppm fluorine
(Creed, 1968). According to Zies (1929), the Valley of
Ten Thousand Smokes, Alaska, at one time produced HF at a
rate of 200,000 tons per year. It is obvious from these
statements that vast quantities of fluorine would be made
available to the hydrosphere wherever and whenever volcanic
activity was extensive.

In addition to volcanic exhalations, large
amounts of fluorine are often released during the later
stages of a differentiating granitic melt. Consequently,
fluorite is characteristic of, and commonly encountered in
(a) pegmatites, (b) pneumatolytic deposits, and (c)
hydrothermal veins. In the case of pneumatolytic deposits
such as greisens and high temperature veins, common mineral
associations with fluorite include cassiterite, topaz,
tourmaline, lepidolite, apatite and quartz. Common mineral
associations with fluorite in late stage hydrothermal
veins include quartz, dolomite, calcite and barite.
Fluorite is also often present in varying quantities as a
gangue mineral with lead and silver ores.

Trace elements such as the rare earths, and
major and minor elements such as K, Na, Ba and Sr can be
present in the fluorite crystal lattice in varying amounts.

Of the rare earths, yttrium, cerium and lanthanum are the
elements most commonly found to substitute for Ca in the
lattice structure. Chatterjee (personal communication, 1977)
reports that a trace element analysis of a sample of
fluorite from the Lake Ainslie area contains one per cent
lanthanum. This may be responsible for the green colouration
observed in the fluorite at this locality.

The rare earth content of fluorites has been
used in attempting to determine the source of mineralizing
fluids by equating high contents with igneous sources and
low contents with amagmatic sources. Studies by Smith (1974)
on the North Pennine orefields, England, included trace
element analyses of 690 fluorites of various origins, the
results from which he determined the North Pennine fluorite
to be of amagmatic origin on the basis of a high yttrium
content (120-915 ppm). These results are in aggreement with
conclusions reached from studies on the origin of the North
Pennine orefields by Sawkins (1966) and Dunham (1966).

In summation, both endogenically and exogenically
derived fluorine are important in the formation of extensive
deposits of fluorite. In the exogenic cycle, the clay
minerals (bentonite in particular) are good holding minerals
for fluorine which can be mobilized, migrate and precipitate
as fluorite under favourable physico-chemical conditions.
The anomalous quantities of fluorine observed in modern
lacustrine brines also suggests that exogenically derived
syngenetic fluorite deposits are also a possibility to be
considered. Epigenetic fluorite deposits of amagmatic
origin (exogenically derived) have been noted in many
instances--most notable of which may be the fluorite in
the North Pennine ore fields in England.

Fluorite deposits derived from endogenic sources
are probably more common than those derived from exogenic
sources--particularly in areas where igneous activity was
extensive. The fluorine in these deposits generally
originates from volcanic exhalations or volatiles associated
with differentiated igneous intrusions.