

CELESTITE IN CENTRAL ONTARIO

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Strontium minerals occur in several different veins in central Ontario; most commonly as gangue minerals but occasionally in sufficient quantity to have economic possibilities. At Galetta, west of the City of Ottawa, barytocelestite, $5\text{BaSO}_4 \cdot \text{SrSO}_4$, is associated with calcite in a vein that is being worked for lead.¹ Well formed crystals of celestite are found at the old Frontenac lead mine north of Kingston. Tabular crystals and fibrous aggregates up to several feet in diameter occur in veins associated with fluor spar in the Madoc district, north of Belleville. Two other localities for celestite are at Lyndhurst on the Brockville-Westport branch of the Canadian National Railway and in the neighborhood of Verona, north of Kingston.

Of a slightly different type is the celestite found near Calabogie² on the Kingston-Pembroke branch of the Canadian Pacific Railway. It takes the form of slab-like masses enclosed in brown dolomite and it seems probable from field evidence that the strontium-bearing solutions were ascending and had their origin in an intrusive diabase dike. The larger masses of celestite have a vein-like character and it is possible that the deposit assumes, in depth, true vein form.

In the vicinity of Kingston celestite occurs in segregations or nodular masses in the Paleozoic limestone, radially fibrous aggregates being common in addition to the tabular crystal form. The limestone belongs to the Black River group. At Kingston it is very fine grained and compact; in places almost lithographic in quality. The celestite nodules are nowhere connected with any veins in this locality, and this is suggestive of Uglow's conclusion³ that the calcite-barite-fluorite-galena veins of this district were formed by the mingling of meteoric and magmatic waters. Strontium would thus be leached from the sediments and added to the ground water circulation.

The present investigation was undertaken mainly to determine whether the strontium in the limestone is present in forms other

¹ E. L. Bruce and Margaret Light, *Am. Mineral.*, Vol. 12, 1927, p. 396.

² H. S. Spence, Barium and Strontium in Canada, *Mines Branch, Dept. of Mines, Ottawa*, p. 80.

³ W. L. Uglow, *Ont. Bur. Mines*, Vol. 25, part 2, p. 40.

than that as celestite in nodules. If it could be shown that strontium occurs as the carbonate or as disseminated celestite in the limestone it would indicate that the strontium found in the vein filling minerals might have come from vadose solutions percolating through the limestone and tend to corroborate the hypothesis that the lead-zinc veins were in part at least due to meteoric waters. The methods employed and the results obtained are here presented.

It is notable that, although strontium sulphate is practically insoluble in acids, it is appreciably soluble in water. Thus a given volume of water will dissolve approximately thirteen times as much SrSO_4 as SrCO_3 , and more than twice as much SrSO_4 as CaCO_3 .

100 parts of water will dissolve,⁴ $\left\{ \begin{array}{l} .0144 \text{ parts of } \text{SrSO}_4 \text{ at } 18^\circ\text{C} \\ .0011 \text{ " " } \text{SrCO}_3 \text{ " } 18^\circ\text{C} \\ .0065 \text{ " " } \text{CaCO}_3 \text{ " } 20^\circ\text{C} \end{array} \right.$

These figures may be used for the natural substances without serious error. Waters percolating through limestone, however, are more or less carbonated, and this would tend to lessen the solubility of celestite or prevent its solution altogether. An alternative possibility is that the carbonated waters might convert the sulphate to the carbonate, in which form it is quite soluble. (100 parts of CO_2 water dissolve 0.12 parts of SrCO_3 ⁴). This would involve a later change to the sulphate before its deposition in the nodules or in the veins as celestite.

Celestite is prepared for analysis by boiling for an hour or more in a concentrated solution of sodium carbonate. This changes strontium sulphate completely to the carbonate. Barium sulphate is only partly converted to the carbonate even under the most favorable conditions and fusion must be carried out to prepare it for analysis. Celestite is not converted to carbonate in a fusion. In every case a residue was found insoluble in HCl and it was evident that the mineral had not been attacked or only partially decomposed.

There is difficulty also in making a complete reduction of strontium oxalate to oxide, and, even when using the purest sample, results as low as 43 per cent for SrO were obtained. The use of a smaller sample would probably permit of complete reduction but this would lessen the accuracy of the minor constituents to be

⁴ Hodgman and Lange, *Handbook of Chem. and Physics*, 13th edition.

determined. A satisfactory alternative is to convert the oxalate to sulphate and weigh it as such. Hillebrand does not mention this method but it is noted in other standard quantitative texts.

A two-gram sample of limestone was taken for analysis and it was found impossible, satisfactorily, to ignite the large oxalate precipitate to oxide. As it was essential to test for strontium, a smaller sample could not be used so that conversion to sulphate was the only alternative.

Although completed analyses have not been made of either celestite or the associated limestone, the following procedure has been tested rather thoroughly and should be applicable where strontium is to be determined in the presence of the common elements associated with strontium.

When a sample is boiled in a concentrated solution of sodium carbonate, calcium, strontium, magnesium, and part of the barium are converted to carbonates, while iron, silica, aluminum and most of the barium are not attacked. Hydrochloric acid dissolves from this residue calcium, strontium, the barium present as carbonate, magnesium, iron and aluminum, leaving silica and barium sulphate undissolved. From this chloride filtrate, in the presence of ammonium chloride, ammonia precipitates iron and aluminum as hydroxides. Calcium and strontium are then separated from barium and magnesium by precipitation in an ammonium oxalate solution. This precipitate is treated with sulphuric acid and the combined sulphates of calcium and strontium are weighed. They are then converted to carbonates in boiling sodium carbonate solution, dissolved in nitric acid, and evaporated to dryness. Calcium is separated from strontium in 1:1 alcohol-ether mixture, the precipitate of calcium being collected in a Gooch crucible and determined as nitrate. The amount of strontium can then be found by difference.

The above is simply an outline of the method employed without details of procedure.

Repeated tests following this method failed to reveal in the limestone any trace of either strontium carbonate or sulphate other than the segregated masses of celestite.

Kraus⁵ has described the celestite from an island in Put-in-Bay in Lake Erie and from a study of the surrounding rocks considers

⁵ E. H. Kraus, *Amer. Jour. Science*, Vol. 19, 1905, p. 286.

that the concentration of celestite is the result of leaching of strontium-bearing sediments. Other localities described from Michigan are of the same type. In these occurrences, however, it is evident that the celestite was originally deposited in small disseminated crystals in the sediments for the leached rock is pitted and distinctly porous.

In contrast, the Kingston celestite occurs in nodular masses six inches or more across and not in small disseminated crystals. The celestite nodules give no evidence of having filled cavities, for the crystals are in compact masses, and, as far as examined, have left no interstitial openings. The chemical data obtained show no dissemination of strontium in the limestone although more refined methods of analysis might disclose its presence. There is, therefore, no proof of the secondary nature of the celestite nodules.

In conclusion, it may be said that this investigation does not support Uglow's hypothesis but since the results are negative and no other source of the strontium in the veins has yet been proved, the assumption of a meteoric source for the strontium solutions must still be considered possible.