The ORE BIN
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The following two articles on the mineral clinoptilolite are significant from three standpoints: (1) the possible start of a new mining operation in Oregon; (2) the ever-widening use of minerals by science and industry today; and (3) the value of geologic mapping.

Clinoptilolite was no more than a mineralogical curiosity prior to the recent discovery of its usefulness for extracting cesium from radioactive wastes. It will be seen from reading the report by Randall E. Brown that its use could well be of great significance in helping to reduce pollution from nuclear reactors. This new application of a mineral is a very sophisticated step from the first use of mineral products by early man, who employed stones to get food and to protect him from his enemies.

The discovery of an important use for this heretofore unnoteworthy mineral exemplifies how difficult it is to evaluate realistically the mineral resources of an area. What new turn science and technology will take next and what their demands on the mineral industry will be is impossible to predict. If clinoptilolite, as it occurs in Oregon, is found suitable for the purposes described by Mr. Brown, there apparently is an enormous reserve in our state, since its host formation, the John Day tuff beds, are distributed over many thousands of square miles in central Oregon.

It is fortunate that research on the mineralogy of these beds had been done by Prof. R. V. Fisher, for without this knowledge the initial inquiry from the General Electric scientists at Hanford could not have been answered by affirmative action.

Hollis M. Dole

THE USE OF CLINOPTILOLITE

By Randall E. Brown*

Clinoptilolite**, a common but generally unrecognized zeolite mineral closely akin to heulandite, may be one answer to a vexing problem of the nuclear industry. That is waste disposal. Clinoptilolite's value lies in its ability to adsorb radioactive cesium from liquid solutions, so that the effluent can in some cases be safely discharged to the environment. Clinoptilolite then may provide the following opportunities for use: (1) a means

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**Pronounced Cly-no-ty'-lo-lite.

of removing radiocesium from wastes for more efficient and economical storage, (2) a means of isolating radiocesium in a solid form for safe storage, and (3) a form for shipping cesium to a storage or processing site.

Many radioactive waste streams are concentrated solutions of primarily non-radioactive salts used in chemical separations processes. Radioactive elements are chemically only trace concentrations although they pose greater disposal problems than the non-radioactive elements. Removal of the radioisotopes from high-salt wastes by normal precipitation reactions or exchange processes often is defeated by competition from the nonradioactive ions. Much of the reaction in such cases involves ions of little or no concern.

Some minerals have an affinity or selectivity for specific ions, probably because of a coincidence of size and charge of the ion and an approximate dimension of the mineral lattice. Thus, in addition to the external surface area available for adsorption, some clays and zeolites possess a large adsorption capacity on internal surfaces. Competition by non-radioactive ions for available deposition sites there is minimized. To date, the affinity of clinoptilolite for cesium appears the most important. Cesium-137, a fission product isotope prevalent in radioactive wastes, has a 30-year half-life and a low permissible body burden. Its removal from wastes and concentration in solids for maximum containment is highly desirable.

Test performance of clinoptilolite

The potential use of clinoptilolite in decontaminating radioactive wastes of Cs^{137} was first recognized by Ames (1,2) in 1959, in studies with clinoptilolite from Hector, California. Its application in permitting disposal of effluents to the environment was quickly recognized. Subsequent work by Ames, Nelson, Mercer, Haney and Honstead (3,4,5,6) demonstrated the selectivity and applicability of clinoptilolite over a wide range of conditions and for a wide variety of waste solutions. Honstead, Ames, and Nelson(6), for instance, described some laboratory experiments with simulated low-level wastes as follows:

> "...a bed of the mineral received more than 50,000 bed volumes of 'waste' and gave no cesium breakthrough. The solution used was ordinary tap water (containing 24 p.p.m. calcium, magnesium and sodium) traced with Cs^{137}. The influent was charged at a flow rate of 3 gal/ft^2 per min. The cesium capacity of the mineral in this case was more than 30 times that of the best non-specific commercial ion-exchange resin which we have examined."

Appreciable strontium decontamination of wastes was also recognized in the Hanford experiments and is ascribed in part to a replacement reaction with a small amount of calcite present in the ore. Other radioisotopes were also removed from the waste in varying degrees, probably because they reacted with impurities (montmorillonite, plagioclase feldspar, mica) and the external surfaces of the clinoptilolite.

Mathers and Watson (7) of Chalk River, Canada, extended some of the Hanford tests and achieved comparable results with higher level wastes. Two tons of clinoptilolite were used to concentrate 400 curies of Cs^{137} and 300 curies of Sr^{90} from 8200 liters of solution. The clinoptilolite, previously crushed, screened, elutriated and acid-washed, presumably contained no calcite, but achieved appreciable decontamination of Sr^{90}.

Clinoptilolite will also concentrate the Cs^{137} from high-level wastes to reduce its storage volume. Honstead, Ames, and Nelson (6) report that the cesium from 27 to 31 bed volumes of high-level waste was concentrated on a clinoptilolite bed. Neutralized high-level wastes, because of the high content of sodium salts, cannot be reduced to this volume even by evaporation to complete dryness. Moreover, indications are that clinoptilolite, a silicate, will not be adversely affected either by the radiation or heat generated by the amount of Cs^{137} that can be concentrated on it.

The concentration of cesium on clinoptilolite then offers another opportunity for use. The bed or column, suitably encased, can serve as a shipping container for subsequent storage or recovery of the cesium for commercial use. The cesium can be readily leached from the clinoptilolite by chemical treatment and the clinoptilolite regenerated. Preliminary tests indicate little degeneration with repeated cycling. The leach rate of cesium from clinoptilolite by water is, advantageously, from 1/2 to 1/10 that of cesium from some tested synthetic exchange materials. Should a container of clinoptilolite become involved in an accident, the cesium will be eluted at a slower rate than from other tested products.

Preparation and beneficiation of clinoptilolite

Clinoptilolite forms in large part by alteration of volcanic glass at low temperatures(8). It accordingly has been found throughout the western United States where volcanic tuffs were deposited and subsequently altered. Tonnages available are huge. However, the chemical composition and physical properties of clinoptilolite, including cesium capacity and specificity, undoubtedly vary greatly from deposit to deposit, bed to bed, and even within a bed. Fortunately, clinoptilolite in some instances forms nearly monomineralic deposits of considerable regularity. Concentrations of 80 to more than 95 per cent are not unusual. Where this occurs, the clinoptilolite need only be crushed and ground to a 10- to 50-mesh size range, screened and washed. This size range permits suitable flow-through rates and maximum use of the cesium capacity.

Mathers and Watson, and Hanford researchers, found that extensive washing and acid treatment is necessary for ores containing carbonate and water-soluble salts. Acid wastes attack the carbonates, cause gas evolution and the release of fine particles of clay and clinoptilolite, evidently held by the carbonates and salts. The fines slowly decrease the flow rate (or increase the pressure drop) and change the operating characteristics of the column prior to optimum cesium saturation. Clinoptilolite itself is markedly acid resistant compared to tested synthetic zeolites; hence, it is usable over a wider range of pH values.

Friable ores that break to smaller than 50-mesh size or that disintegrate with use because of the impurities may be finely ground and pelletized. Careful selection of the binder is important to maintain the clinoptilolite selectivity adsorption and kinetics, particularly with acid waste streams. Synthesis of clinoptilolite also is promising. However, the best or ideal clinoptilolite is not yet defined; indeed several varieties may be necessary for different waste streams. Attempts to synthesize clinoptilolite have resulted in the formation of similar or related minerals rather than clinoptilolite(9). This suggests that clinoptilolite may be comparatively unstable, or at least that its relationships to analcite, heulandite, and montmorillonite are not yet adequately understood.

Conclusions

Clinoptilolite possesses characteristics potentially of value to the nuclear industry. Conceivably, these characteristics may be the basis of a new mining industry that would include other minerals that are specific for radioisotopes other than cesium. These minerals can not be regarded as a panacea for nuclear waste problems, but they are an important addition to waste-treatment methods available for consideration.

The work outlined in this report was performed under Contract No. AT(45-1)-1350 between the Atomic Energy Commission and General Electric Co.

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CLINOPTILOLITE TUFF FROM THE JOHN DAY FORMATION, EASTERN OREGON

By Richard V. Fisher*

A lenticular but persistent coarse-grained tuff composed almost exclusively of zeolitized shards occurs within the middle member of the John Day Formation, Picture Gorge quadrangle, of eastern Oregon. The zeolite which replaces the original glass of the shards is clinoptilolite, a sodium- and silica-rich variety of heulandite. This zeolite is of interest because of its ability to capture Cesium-137 from radioactive waste products.

The map area is located in the north-central part of the Picture Gorge quadrangle in Wheeler and Grant Counties, Oregon (Ts. 10 and 11 S., Rs. 25 and 26 E.). Accessibility to exposures of the map area is easy from Oregon Highway 19, which bisects the Picture Gorge quadrangle (see geologic map, pages 200 and 201).

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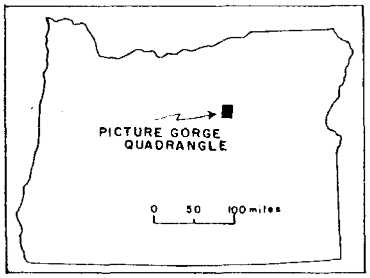

The Deep Creek Tuff, so named for thick exposures in the vicinity of Deep Creek, is composed of more than 95 percent shards altered to clinoptilolite. It varies in thickness from one or two feet to as much as 25 feet in comparatively short distances within the central part of the Picture Gorge quadrangle. Exposures of the tuff occur in Kahler Basin (secs. 33 and 27, T. 7 S., R. 25 E.) and in the Sheep Rock area some 30 miles south of the Kahler Basin exposures. It has been observed in the Rudio Creek area (sec. 6, T. 10 S., R. 27 E.), about 6 miles east of the map area, and about 17 miles west of Rudio Creek within the Richmond quadrangle. Its minimum extent, therefore, is about 500 square miles, but doubtless extends over a far wider area. A similar thick tuff layer within about the same stratigraphic horizon crops out near Logan Butte some 50 miles to the south.

This report is an outgrowth of a study being conducted on the John Day Formation under National Science Foundation Grant No. G18642.

Stratigraphy

The John Day Formation (Oligocene? to lower Miocene) was originally divided into a lower, a middle, and an upper member by Merriam (1901). Coleman (1949) in the Picture Gorge quadrangle agreed with this general subdivision. Fisher and Wilcox (1960) in the Monument quadrangle also recognized three major members, but used slightly different stratigraphic criteria for delimiting them. Current mapping by the writer in the Kimberly and Picture Gorge quadrangles extends these members westward from the Monument quadrangle.

The John Day Formation is overlain unconformably by a thick sequence of Picture Gorge Basalt*, and south of the map area lies unconformably on Cretaceous (?) sedimentary and pre-Cretaceous (?) metamorphic rocks. Deep red volcanic siltstones of the lower member do not crop out in the map area, but, since they occur within slide blocks immediately south, they probably are not far below the prominent green-colored John Day exposures in NE$\frac{1}{4}$NE$\frac{1}{4}$ sec. 6, T. 11 S., R. 26 E.

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*Waters (1961) recognizes sufficient variation in the lithology of Columbia River Basalt to segregate two mappable units, the lower one of which he calls "Picture Gorge Basalt."

The green beds of the middle member, as much as 700 feet thick in the map area, are fine- to coarse-grained tuffs composed of shards and pumice fragments altered to zeolite and clays. Predominating crystals are sodic plagioclase, clinopyroxene, and magnetite. Green colors are caused by the secondary clay minerals, celadonite, and iron-rich montmorillonite. Coarse-grained tuffs within the section, except for the Deep Creek Tuff, are invariably mixed with abundant fine-grained clays.

The upper member of the formation, about 100 feet thick within the map area, is composed of massive gray volcanic siltstones overlain by cross-bedded sandstones and conglomerates. These rocks contain glass shards slightly altered to gray montmorillonite. In places, the erosion surface above the John Day Formation cuts through the formation and the overlying basalts rest directly upon the middle member.

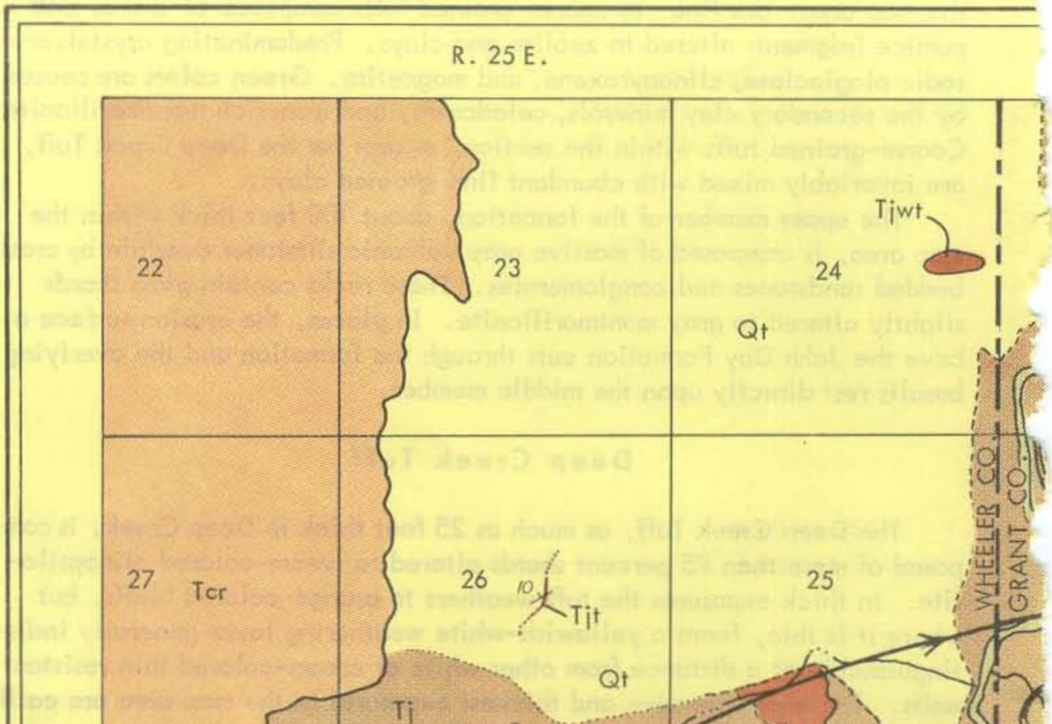
Deep Creek Tuff

The Deep Creek Tuff, as much as 25 feet thick in Deep Creek, is composed of more than 95 percent shards altered to cream-colored clinoptilolite. In thick exposures the tuff weathers to orange-colored bluffs, but where it is thin, forms a yellowish-white weathering layer generally indistinguishable at a distance from other white or cream-colored thin resistant units. The most extensive and thickest exposures in the map area are easily accessible and visible from Oregon Highway 19.

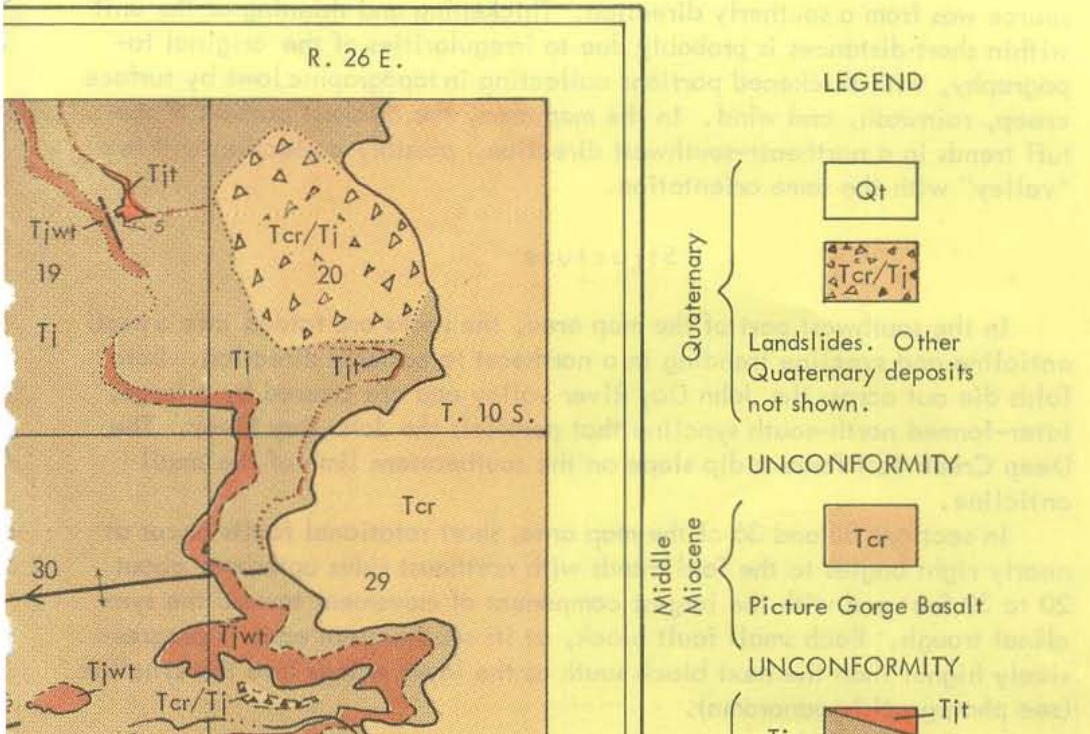
The lower contact of the tuff, observed at NE$\frac{1}{4}$ sec. 19, T. 10 S., R. 26 E., is texturally gradational downward within a few inches to medium- and fine-grained tuff typical of the middle member. This contact is somewhat irregular in detail but on the whole is relatively even. Its contact with overlying rocks has not been observed.

The tuff is generally massive without distinctive laminae, and consists of large interlocking shards with minor amounts of lithic fragments and plagioclase crystals. The lithic fragments, usually less than a millimeter in longest dimension, are equant, varicolored extrusive rocks, and generally form thin, one- to two-inch laminae grading into massive tuff. In Squaw Creek, S$\frac{1}{2}$ sec. 14, T. 11 S., R. 25 E. a few miles south of the map area, at least three zones of graded laminae occur and some of the tuff is platy. There, the lithic fragments are larger and form a more prominent part of the tuff than in the present area.

The Deep Creek Tuff is an ashfall tuff formed from a single episode of explosive volcanism. At least three and possibly more eruptions took place, as evidenced by graded laminae in Squaw Creek south of the map area and platiness within the upper part of the tuff in NE$\frac{1}{4}$ sec. 19, T. 10 S.,R.26E.



Geologic map showing distribution of



inoptilolite tuff.

The tuff is coarser in Squaw Creek than in the map area, suggesting that its source was from a southerly direction. Thickening and thinning of the unit within short distances is probably due to irregularities of the original topography, with thickened portions collecting in topographic lows by surface creep, rainwash, and wind. In the map area, the thickest portion of the tuff trends in a northeast-southwest direction, possibly collecting within a "valley" with the same orientation.

Structure

In the southwest part of the map area, the rocks are folded into a small anticline and syncline trending in a northeast to easterly direction. Both folds die out across the John Day River valley and are crossed by a large, later-formed north-south syncline that parallels the John Day River. The Deep Creek Tuff forms a dip slope on the southeastern limb of the small anticline.

In sections 35 and 36 of the map area, short rotational faults occur at nearly right angles to the fold trends with northeast sides upthrown about 20 to 30 feet and with the largest component of movement toward the synclinal trough. Each small fault block, at its southeastern end, is progressively higher than the next block south as the layer swings into the syncline (see photographic panorama).

Summary

The Deep Creek Tuff in most thick outcrops is remarkably homogeneous and remarkably rich in clinoptilolite. Easily accessible exposures in sec. 19, T. 10 S., R. 26 E. on the east side of the river occur as terrace-like cappings on softer John Day rocks. Exposures in Deep Creek on the W-4 Ranch (secs. 35 and 36, T. 10 S., R. 25 E.) are far more extensive in area and, together with the above-mentioned locality, form many acres of almost pure clinoptilolite available for strip mining along a paved highway.

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↑ Photograph showing small, gentle syncline and step faults in its trough. Rock layer capping terraces in foreground is Deep Creek Tuff. Dip slope on southeast limb of anticline as marked. John Day Formation shows as light-colored slopes beneath darker layers of capping Picture Gorge Basalt. View is north down John Day River valley, toward the town of Kimberly.

← Massive bed of Deep Creek Tuff showing gradation downward into finer grained middle member at NE¼ sec. 19, T. 19 S., R. 26 E.

RUSSIANS REPORTED DUMPING CHROME ORE IN U.S.

The Russians have launched what producers term economic warfare in chrome ore. It has been estimated that between 70,000 to 100,000 tons have entered the U.S. over the last three months at prices far below production costs (i.e.$15.50 l.t. for chemical grade). It is rumored that the U.S. trading companies importing the ore are doing so under private barter arrangements.

The motive behind the Russian action is unknown, but the effect is clear. Free World producers maintain they will not long be able to keep their mines operating in the face of such unfair competition. (E&MJ Metal and Mineral Markets, v. 33, no. 50, Dec. 13, 1962).

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NORTHWEST METALS AND MINERALS CONFERENCE

The 16th annual Pacific Northwest Metals and Minerals Conference will be held in Portland at the Multnomah Hotel, April 25-27, 1963. The conference will be sponsored jointly by the American Institute of Mining, Metallurgical, and Petroleum Engineers; the American Society for Metals; the American Welding Society; and the National Association of Corrosion Engineers. Technical sessions on Thursday and Friday will be divided into Minerals Branch and Metals Branch programs. Field trips to local metallurgical plants and testing laboratories and a full social schedule round out the conference program.

The success of the first Gold and Money Session, when the conference was last held in Portland in 1960, has prompted a second meeting, with Hollis M. Dole as chairman and Pierre Hines, vice-chairman. Speakers for the Gold and Money Session include: Evan Just, Head of the Department of Mineral Engineering, Stanford University; Henry Hazlitt, Contributing Editor, Newsweek Magazine; John Exter, Senior Vice-President of the National City Bank of New York; and Dr. W. J. Busschau, Chairman, Gold Fields of South Africa, Ltd. Donald H. McLaughlin, Chairman of the Homestake Mining Co., will act as moderator for the panel session on Friday afternoon. The high calibre of the Gold and Money speakers has already attracted considerable attention in gold-mining and financial circles.

Technical sessions will be devoted to a wide variety of subjects, including nuclear metals, space-age and missile metals, semi- and superconductors, the wake (or wake-up) of the domestic mining industry, transportation of industrial minerals, stockpiling of nickel, lunar geology, oceanographic prospecting, and opportunities for the small miner. Central theme for the conference, which rotates between Portland, Spokane, and Seattle annually, is SENT - Science, Engineering, New Technologies. Harry Czyzewski of Metallurgical Engineers, Inc., is general conference chairman.

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TAX COMMISSION STUDY

The State Tax Commission has just completed a study on the taxation of severed mineral interests. The study by Donald H. Burnett, Assistant Attorney General assigned to the Tax Commission, reviews the taxation of mineral deposits of 34 states and discusses alternatives that might be explored in correcting the difficult administrative problems arising from Oregon's present system of ad valorem taxation of severed mineral interests. The study is 21 pages in length, with an 18-page appendix summarizing the 34 taxation laws. It includes Opinion 5441 by the Attorney General, which states that reserved mineral interests must be separately listed and assessed for tax purposes. The State Tax Commission's office is 412 State Office Building, Salem 10, Oregon.

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LIME PLANT TO BE BUILT IN PORTLAND AREA

Ash Grove Lime & Portland Cement Co. of Kansas City, Missouri, one of the oldest producers of burnt lime in the United States, has announced plans to erect a $3.5 million plant in the River Gate Industrial Center in the St. Johns district of Portland. The plant will have a capacity of 250 tons of lime daily. Raw material will be barged in from Texada Island, British Columbia, the same source from which Oregon Portland Cement Co. gets limestone for its Oswego cement plant.

Ash Grove plans to manufacture a complete line of burnt and hydrated lime products for existing and potential basic industries in the area. Approximately 35 persons will be employed when the plant is completed early in 1963. The new plant will be the second lime producer in the state. Chemical Lime Co. at Baker has been producing a high-quality chemical lime from limestone quarried at nearby Marble Mountain for the past 5 years.

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RECORD YEAR FOR CANADIAN EXPLORATION

This has been a record year for prospecting and exploration activity in Canada's Pacific Northwest, Thomas Elliott, manager of the British Columbia & Yukon Chamber of Mines, disclosed at the Northwest Mining Association Convention in Spokane. He said Canada's mining laws have a great deal to do with this by offering the maximum amount of encouragement both to the individual prospector and the large company.

Some 500 prospectors were active in search for new mineral deposits, he said. Many were employed by the 50 exploration companies that are spearheading the intensive program at a cost of about $5 million each year.

Twenty-five helicopters, in addition to numerous airplanes, were used to transport men and materials into isolated sections of the country, he said.

Some 50 prospectors received financial assistance under the British Columbia Prospectors' Grubstake Act and 23 two-men parties in the Yukon were given aid under a new program introduced by the Department of Northern Affairs & National Resources, Ottawa, he said.

More than 16,000 mining claims were recorded in British Columbia in the first 10 months of this year, he said.

This also has been a successful year from the standpoint of new discoveries, he said. One of the "most significant mineral discoveries ever made in Western Canada" was the finding of a large sedimentary deposit of hematite iron ore in Yukon's Snake River area, he said.

British Columbia mineral exports to Japan continue to grow, he said, and are expected to total $40 million this year. (Wallace Miner, Dec.6, 1962)

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DEPARTMENT PUBLISHES BIBLIOGRAPHY SUPPLEMENT

"Bibliography of the Geology and Mineral Resources of Oregon, Third Supplement," has been published by the department as Bulletin 53. It covers the 5-year period from January 1, 1951, to December 31, 1955. The compilers, Margaret L. Steere and Lillian F. Owen, have included all available published and unpublished reports on Oregon geology and mineral resources for this period. The 97-page bulletin contains, in addition to the bibliography, a list of the sources consulted and a subject index. Bulletin 53 may be obtained from the department's offices in Portland, Baker, and Grants Pass. The price is $1.50 postpaid.

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