

## DETECTION OF NICKELIFEROUS ROCKS BY ANALYSIS OF HERBARIUM SPECIMENS OF INDICATOR PLANTS

R.R. BROOKS<sup>1</sup>, J. LEE<sup>1</sup>, R.D. REEVES<sup>1</sup> and T. JAFFRÉ<sup>2</sup>

<sup>1</sup> Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North (New Zealand)

<sup>2</sup> Centre O.R.S.T.O.M., Nouméa (New Caledonia)

(Received June 24, 1976; revised version accepted October 18, 1976)

### ABSTRACT

Brooks, R.R., Lee, J., Reeves, R.D. and Jaffré, T., 1977. Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *J. Geochem. Explor.*, 7: 49-57.

Nearly 2000 herbarium specimens and 232 species of the genera *Homalium* and *Hybanthus* were analysed for nickel in order to identify plant accumulators of nickel which were indicative of nickeliferous (usually ultrabasic) rocks. The specimens were originally collected from all parts of the tropical and warm-temperate World between latitudes 40° N and 40° S. They represented a sampling density of about 1 specimen per 2000 km<sup>2</sup>. The survey resulted in the re-identification of all previously known hyperaccumulators (>1000 µg/g on dry-weight basis) of nickel (five species) and in the discovery of five additional species (all from New Caledonia) from these two genera.

Fourteen previously unknown strong accumulators (100-1000 µg/g) of nickel were also discovered, most of which were growing over ultrabasic rocks.

From the collection localities of the accumulators, it was possible to pinpoint many of the World's major ultrabasic areas in warm temperate and tropical regions. The principle of the method should be applicable to other genera and other elements.

### INTRODUCTION

Because the elemental content of most plants reflects to some extent the nature of the substrate on which they are growing, inorganic analysis of plant material is of importance to geologists, biogeochemists and exploration geochemists. Such analyses have been used to locate mineral deposits and to identify areas potentially favourable for the discovery of certain types of mineralization (Brooks, 1972; Malyuga, 1964). Ultrabasic rocks, which are characteristically high in nickel, are of considerable importance because they are often hosts for economic deposits of nickel, chromium, platinum and other metals.

Relatively few plants are able to accumulate concentrations of nickel

O. R. S. T. O. M.

5 AVR. 1977

Collection de Référence

Collection de Référence

n° 8585 M

BBV

exceeding 15  $\mu\text{g/g}$  on a dry weight basis, unless they are growing over ultra-basic rocks, in which case nickel concentrations of 25–50  $\mu\text{g/g}$  may be found (Lyon et al., 1970). Values above 100  $\mu\text{g/g}$  are uncommon, even for an ultra-basic environment, and values exceeding 1000  $\mu\text{g/g}$  are restricted to a small group of highly unusual plants which may be termed *hyperaccumulators*. The term hyperaccumulator is used in this report to refer to the concentration in the plant, irrespective of the concentration in the substrate.

The already published list of hyperaccumulators of nickel now including eleven species: *Alyssum bertolonii*\* (Minguzzi and Vergnano, 1948); *Dicoma macrocephala* (Wild, 1970); *Dicoma niccolifera* (Wild, 1971); *Geissois pruinosa* and *Homalium guillainii* (Jaffré and Schmid, 1974); *Homalium kanaliense*, *Hybanthus austrocaledonicus* and *Hybanthus caledonicus* (Brooks et al., 1974); *Hybanthus floribundus* (Severne and Brooks, 1972; Cole, 1973); *Psychotria douarrei* (Jaffré and Schmid, 1974); *Sebertia acuminata* (Jaffré et al., 1976). Except for the two *Dicoma* species (Rhodesia), *H. floribundus* (Australia) and *A. bertolonii* (Italy), all these hyperaccumulators are from New Caledonia.

The interest in nickel hyperaccumulators has arisen partly because of their possible significance in mineral exploration and partly because of the interesting problems in plant chemistry and physiology presented by high accumulations of an element which is normally toxic to vegetation at such concentrations.

The presence of several species of the genera *Homalium* and *Hybanthus* in the list of hyperaccumulators, raises the question as to whether this nickel-accumulating ability is a world-wide characteristic of these genera, or whether it is confined to New Caledonian and Australian species. The World's herbaria contain well over 200 million plant specimens which have been collected over the past 150 years, and which to date have seldom been used for other than taxonomic purposes.

Analysis of herbarium specimens would be a simple, rapid and inexpensive method of carrying out such a world-wide survey but very little work of this nature seems to have been done in the past. Some years ago, Persson (1956) analysed the soil attached to herbarium specimens of "copper mosses" to detect cupriferous localities in Sweden. Cole (1971) identified cuprophytes over a copper deposit in southern Africa and checked herbarium sheets for collection localities of other specimens of these species without actually analysing herbarium material. It appears that the only record of the analysis of phanerogams from herbaria is the work of Chenery (1948) who carried out an analysis for aluminium in over 4000 herbarium specimens. His method was, however, semi-quantitative and required a leaf sample of over 6  $\text{cm}^2$  in area. More recently, Goodman and Roberts (1971) analysed bryophytes from herbaria to monitor atmospheric pollution. The paucity of work involving analysis of herbarium material probably reflects the fact that it is only in recent years that instrumentation has progressed far enough to allow for the

\* Probably identical with *A. murale* (Malyuga, 1964).

analysis of samples sufficiently small to satisfy the requirements of herbarium curators.

For the work reported in this paper, more than fifty herbaria throughout the World were approached for small samples of leaf material from their collections of *Homalium* and *Hybanthus*. Thirty-five of these institutions (Table I) supplied material.

These samples were analysed for the nickel content in an attempt to find additional nickel accumulators and nickeliferous rocks. Although the nature of the substrate is often unknown for herbarium specimens, studies on known nickel accumulators (Severne and Brooks, 1972; Brooks et al., 1974; Jaffré and Schmid, 1974) have shown that nickel values over 1000  $\mu\text{g/g}$  (dry weight) are only associated with plants growing over ultrabasic rocks. These and other studies showed that values from 100 to 1000  $\mu\text{g/g}$  were invariably associated with ultrabasic areas, except occasionally for plants growing over laterites not overlying ultrabasic rocks, where values of up to 200  $\mu\text{g/g}$  were found. Analysis of a sufficient number of each species of these plants should enable a distinction to be made between nickel levels characteristic of ultrabasic environments and those typical of more acidic substrates.

#### ANALYTICAL PROCEDURES

Dried leaf samples with an average weight of about 0.03 g, (about 1  $\text{cm}^2$ ) were placed in 5- $\text{cm}^3$  borosilicate test-tubes and ignited at 500°C in a muffle furnace. The ash in each tube was then dissolved in 1  $\text{cm}^3$  of 2M hydrochloric acid. The solutions were analysed for nickel by atomic absorption spectrophotometry. Corrections for non-atomic absorption were made by using a hydrogen continuum lamp. All concentration data were expressed on a dry-weight basis. To convert to an ash weight basis all values should be multiplied by 15.

#### RESULTS AND DISCUSSION

##### *General*

The genera *Homalium* (Flacourtiaceae) and *Hybanthus* (Violaceae) comprise approximately 240 and 150 species respectively. The co-operating herbaria provided 1926 specimens for analysis, including 128 *Homalium* and 104 *Hybanthus* species. Because of space limitations, precise collection localities are not given but can be furnished by the authors on request.

Fig. 1 shows those species of which at least one specimen had an anomalously high nickel level ( $>15 \mu\text{g/g}$  dry weight). The figure shows the number of specimens analysed and the range of nickel values found. Any extremely high value differing by more than a factor of two from the remainder of the range is specially indicated by broken lines. Occasionally there are low va-

TABLE I

List of co-operating herbaria

Country	Institution	Address
1. Argentina	Fundacion Miguel Lillo	San Miguel de Tucuman
2. Argentina	Museo de Ciencias Naturales	Buenos Aires
3. Australia	Herbarium Australiense, C.S.I.R.O.	Canberra
4. Brazil	Inst. de Pesquisa Agropecuaria	Belem
5. Brazil	Museo Nacional, Universidade Federal	Rio de Janeiro
6. France	Muséum National d'Histoire Naturelle	Paris F75005
7. Germany	Bot. Garten und Museum	Berlin-Dahlem
8. Germany	Herbarium Haussknecht	Jena (DDR)
9. India	Banaras Hindu Univ.	Varanasi 5
10. India	Blattner Herbarium, St. Xaviers College	Bombay
11. India	Central National Herbarium	Howrah 3
12. India	Central Circle, Bot. Survey India	Allahabad
13. India	Eastern Circle, Bot. Survey India	Shillong 3
14. India	Southern Circle, Bot. Survey India	Coimbatore
15. Indonesia	Herbarium Bogoriense	Bogor
16. Netherlands	Rijksherbarium	Leiden
17. New Caledonia	O.R.S.T.O.M.	Nouméa
18. Philippines	Pambansang Museo	Manila
19. Portugal	Centro Botanico	Lisbon 3
20. Portugal	Instituto Botanico, Univ. of Coimbra	Coimbra
21. Portugal	Instituto Botanico, Univ. of Lisboa	Lisbon 2
22. South Africa	Bolus Herbarium, Univ. of Cape Town	Cape Town
23. South Africa	Botanical Res. Inst., D.S.I.R.	Durban
24. South Africa	Compton Herbarium, Kirstenbosch	Cape Town
25. South Africa	National Herbarium	Pretoria
26. Sweden	Inst. Systematic Bot., Univ. of Uppsala	Uppsala
27. Switzerland	Bot. Garten, Univ. of Zürich	Zürich
28. United Kingdom	Royal Botanical Gardens	Kew
29. United Kingdom	Royal Botanical Gardens	Edinburgh
30. United States	Dept. of Botany, Univ. of California	Berkeley, Calif.
31. United States	Field Museum of Natural History	Chicago, Ill.
32. United States	Missouri Botanic Gardens	St. Louis, Mo.
33. United States	Academy of Natural Sciences	Philadelphia, Pa.
34. United States	New York Botanic Garden	Bronx, N.Y.
35. United States	Univ. of Missouri Herbarium	Columbia, Mo.

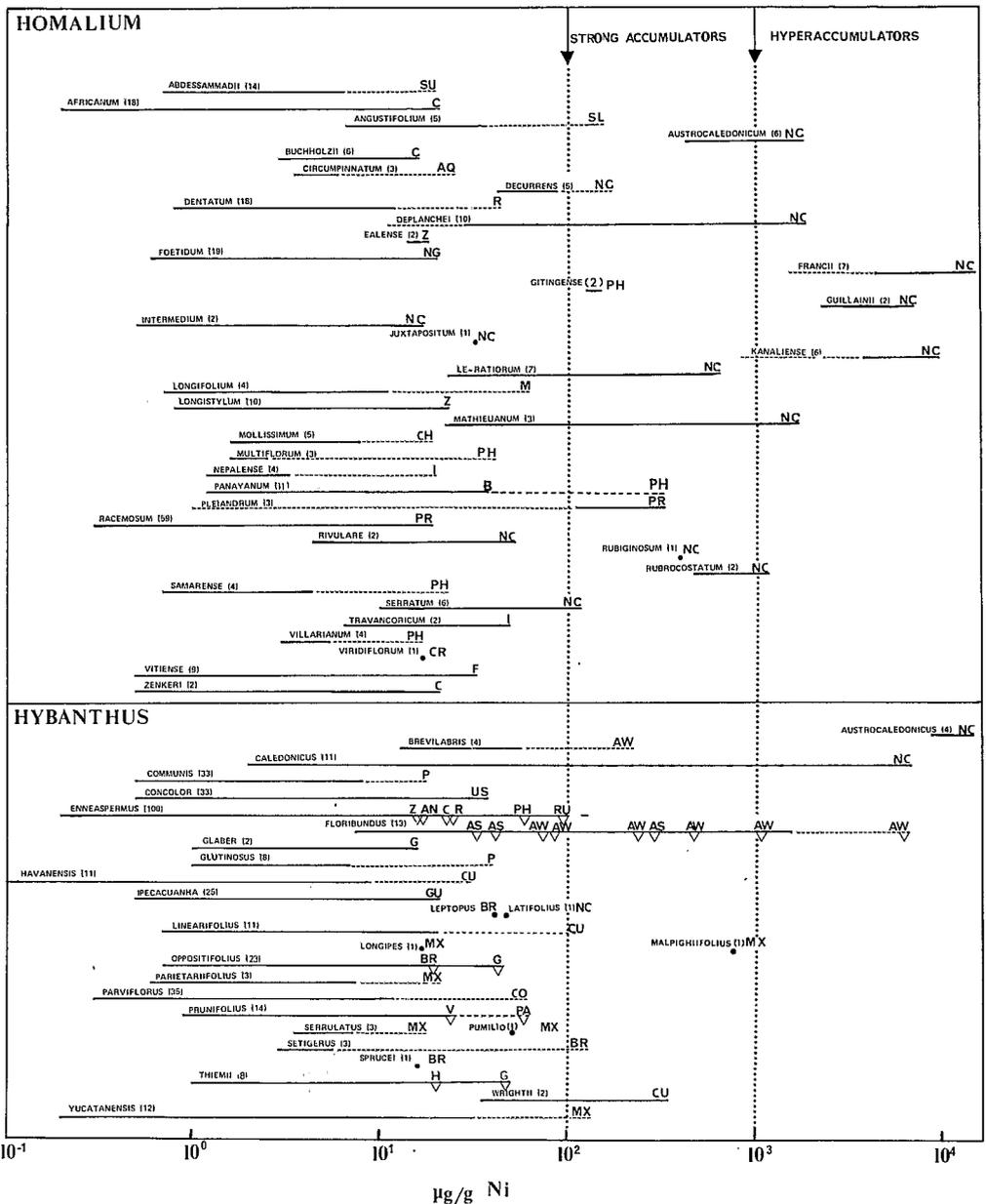


Fig. 1 Range of nickel concentrations ( $\mu\text{g/g}$  dry weight) in *Homalium* and *Hybanthus* species containing at least one value higher than  $15 \mu\text{g/g}$ . Extreme values differing by more than a factor of two from all others are shown by broken lines. For each species, the country or countries of origin of specimens with anomalous values are indicated by the following code: AN = Australia (Northern Territory), AQ = Australia (Queensland), AS = Australia (South Australia), AW = Australia (Western Australia), B = Borneo, BR = Brazil, C = Camerouns, CH = China (Hainan), CO = Colombia, CU = Cuba, F = Fiji, G = Guatemala, GU = Guyana, H = Honduras, I = India, M = Malaya, MX = Mexico, NC = New Caledonia, NG = New Guinea, P = Paraguay, PA = Panama, PH = Philippines, PR = Puerto Rico, R = Rhodesia, RU = Ruanda Urundi, SL = Sierre Leone, SU = Sudan, US = United States, V = Venezuela, Z = Zaire.

lues which are anomalous and these are also shown by broken lines. The figure clearly illustrates the predominance of New Caledonia as a source of hyperaccumulators ( $> 1000 \mu\text{g/g}$ ) and strong accumulators ( $100\text{--}1000 \mu\text{g/g}$ ) of nickel.

#### *Identification of nickeliferous (ultrabasic) substrates*

Tables II and III give additional data for hyperaccumulators and strong accumulators of nickel. All specimens were taken from different sites and where possible, the nature of the substrate was determined from a knowledge of the sample locality.

Although this herbarium survey was carried out at a very low sampling density over a large part of the Earth between the equator and the  $40^\circ$  latitudes, it delineated many of the World's major ultrabasic areas (i.e. Cuba, Puerto Rico, the Philippines, Western Australia and New Caledonia). In the hypothetical case that none of these areas had been known before the survey, it is clear that a number of important finds would have been made. It is therefore not unreasonable to expect that surveys of this nature could be used to delineate previously unknown ultrabasic areas in geologically poorly mapped areas elsewhere.

#### *The discovery of additional nickel-accumulating plants*

This work has resulted in the discovery of five new hyperaccumulators (Table II) and fourteen strong accumulators (Table III) of nickel. The effectiveness of the herbarium survey is further shown by the fact that all previously known hyperaccumulators of nickel were "rediscovered" without the necessity of field work.

Perhaps the discovery of these new nickel-accumulating plants will stimulate fresh research into the ecology and plant chemistry of these species with particular reference to their significance in mineral exploration.

#### *The regional distribution of nickel-accumulating plants*

Tables II and III show the peculiarly regional distribution of nickel accumulators. All the hyperaccumulators of the genus *Homalium* are confined to New Caledonia. Sleumer (1974) has recognized sixteen species of *Homalium* in New Caledonia. Of these, seven were hyperaccumulators and four were strong accumulators. New Caledonia also has two hyperaccumulators of the genus *Hybanthus*.

Outside of New Caledonia, only one other hyperaccumulator (from these genera) is known (*H. floribundus* from Western Australia).

TABLE II

Hyperaccumulators (>1000  $\mu\text{g/g}$  dry weight) of nickel

Species	Total No.	No. above 1000 $\mu\text{g/g}$	Locality	Highest Ni conc. ( $\mu\text{g/g}$ dry weight)	Nature of substrate
<i>Homalium</i>					
<i>australeadonicum</i> Sleum.	6	4	New Caledonia	1805	ultrabasic
<i>deplanchei</i> Warb.	10	2	New Caledonia	1850	ultrabasic
<i>francii</i> Guillaumin	7	7	New Caledonia	14500 <sup>1</sup>	ultrabasic
<i>guillainii</i> Briq.	2	2	New Caledonia	6926	ultrabasic
<i>kanaliense</i> Briq.	6	5	New Caledonia	9420	ultrabasic
<i>mathieuanum</i> Briq.	3	1	New Caledonia	1694	ultrabasic
<i>rubrocostatum</i> Sleum.	2	1	New Caledonia	1157	ultrabasic
<i>Hybanthus</i>					
<i>australeadonicus</i> Schinz et Guillaumin	4	4	New Caledonia	13750	ultrabasic
<i>caledonicus</i> (Turcz.) Cretz.	11	2	New Caledonia	5917	ultrabasic for values >1000 $\mu\text{g/g}$
<i>floribundus</i> F. Muell.	13	2	W. Australia	6680	ultrabasic for values >1000 $\mu\text{g/g}$

TABLE III

Strong accumulators (100–1000  $\mu\text{g/g}$  dry weight) of nickel

Species	Total No.	No. above 100 $\mu\text{g/g}$	Locality	Highest Ni conc. ( $\mu\text{g/g}$ dry weight)	Nature of substrate
<i>Homalium</i>					
<i>angustifolium</i> Keay	5	1	Sierre Leone	155	unknown
<i>decurrens</i> Briq.	5	1	New Caledonia	176	various incl. ultrabasic
<i>gitingense</i> Elmer	2	2	Philippines	144	unknown
<i>le-ratorum</i> Guillaumin	7	4	New Caledonia	643	various incl. ultrabasic
<i>panayum</i> F. Villar	11	1	Philippines	507	ultrabasic
<i>pleiandrum</i> Blake	3	2	Puerto Rico	343	ultrabasic
<i>rubiginosum</i> Warb.	1	1	New Caledonia	397	ultrabasic
<i>serratum</i> Guillaumin	6	1	New Caledonia	116	ultrabasic
<i>Hybanthus</i>					
<i>brevilabris</i> Domin.	4	1	W. Australia	229	ultrabasic
<i>linearifolius</i> Urb.	11	1	Cuba	107	ultrabasic
<i>malpighiifolius</i> Standley	1	1	Mexico	638	unknown
<i>setigerus</i> Baill.	3	1	Brazil	130	probably ultrabasic
<i>wrightii</i> Urb.	2	1	Cuba	350	ultrabasic
<i>yucatanensis</i> Millsp.	12	1	Mexico	134	unknown

## CONCLUSIONS

The survey has been successful in showing that herbarium specimens may be used to discover new accumulator plants, and to indicate areas of specific geology.

There is no reason why the same principles should not be applied to other genera for other elements. In the present survey, the nickel content of vegetation was used to delineate geology. Nickel itself was not the specific target. Mineral deposits of many elements would be too localised for herbarium surveys to be of use. This is not, however, true of some porphyry copper deposits where mineralization can extend over a large area and could possibly be determined by a herbarium survey.

To date, herbaria have been most co-operative in furnishing small samples for this work, but this attitude may well change if inordinately heavy demands are made upon their services. Curators of herbaria have to maintain a fine balance between providing material for research and preserving irreplaceable specimens; this requirement is likely to prove the most serious limiting factor for future surveys of this nature.

## ACKNOWLEDGEMENTS

The authors would like to express their deep appreciation to the 35 herbaria (Table I) who so generously contributed material for this survey.

## REFERENCES

- Brooks, R.R., 1972. Geobotany and Biogeochemistry in Mineral Exploration. Harper and Row, New York, N.Y.
- Brooks, R.R., Lee, J. and Jaffré, T., 1974. Some New Zealand and New Caledonian plant accumulators of nickel. *J. Ecol.*, 62: 493-499.
- Chenery, E.M., 1948. Aluminium in the plant world. *Kew Bull.*, 2: 173-183.
- Cole, M.M., 1971. The importance of environment in biogeographical/geobotanical and biogeochemical investigations. *Can. Inst. Min. Metall. Spec. Vol.*, 11: 414-425.
- Cole, M.M., 1973. Geobotanical and biogeochemical investigations in the sclerophyllous woodland and shrub associations of the Eastern Goldfields area of Western Australia, with particular reference to the role of *Hybanthus floribundus* (Lindl.) F. Muell. as a nickel indicator and accumulator plant. *J. Appl. Ecol.*, 10: 269-320.
- Goodman, G.T. and Roberts, M.T., 1971. Plants and soils as indicators of metals in the air. *Nature*, 231: 287-292.
- Jaffré, T. and Schmid, M., 1974. Accumulation of nickel by a Rubiaceae of New Caledonia. *Psychotria douarrei* (G. Beauvisage) Däniker. *C. R. Acad. Sci. Paris Sér. D.*, 278: 1727-1730 (in French).
- Jaffré, T., Brooks, R.R., Lee, J. and Reeves, R.D., 1976. *Sebertia acuminata*: a nickel-accumulating plant from New Caledonia. *Science*, 193: 579-580.
- Lyon, G.L., Brooks, R.R., Peterson, P.J. and Butler, G.W., 1970. Some trace elements in plants from serpentine soils. *N.Z.J. Sci.*, 13: 133-139.
- Malyuga, D.P., 1964. Biogeochemical Methods of Prospecting. Consultants Bureau, New York, N.Y.

- Minguzzi, C. and Vergnano, O., 1948. The nickel content of the ash of *Alyssum bertolonii* Desv. Botanical and geochemical considerations. *Atti Soc. Tosc. Sci. Nat.*, 55: 49-77 (in Italian).
- Persson, H., 1956. Studies on the so-called "copper mosses". *J. Hattori Bot. Lab.*, 17: 1-18.
- Severne, B.C. and Brooks, R.R., 1972. A nickel-accumulating plant from Western Australia. *Planta*, 103: 91-94.
- Sleumer, H., 1974. A concise revision of the Flacourtiaceae of New Caledonia and the Loyalty Islands. *Blumea*, 22: 123-147.
- Wild, H., 1970. The vegetation of nickel-bearing soils. *Kirkia*, Suppl. to V.7: 1-62.
- Wild, H., 1971. The taxonomy, ecology and possible method of evolution of a new metalliferous species of *Dicoma* Cass. (Compositae). *Mitt. Bot. Staatssamml. München*, 10: 266-274.