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Inorganic Constituents in Australian Coals ²

I. Introduction

In modern coal science there is an increased awareness of the importance of the inorganic constituents in coal, especially as they are often limiting factors in coal utilization.

The annual production of all coals in Australia is about 40 million metric tons, which represents about 45 % of the value of the total mineral production. Most of this coal is used for the generation of electric power and the production of metallurgical coke; there is also an increasing export of coking coal to Japan.

The locations of the main coalfields in Australia are shown in Fig. 1.

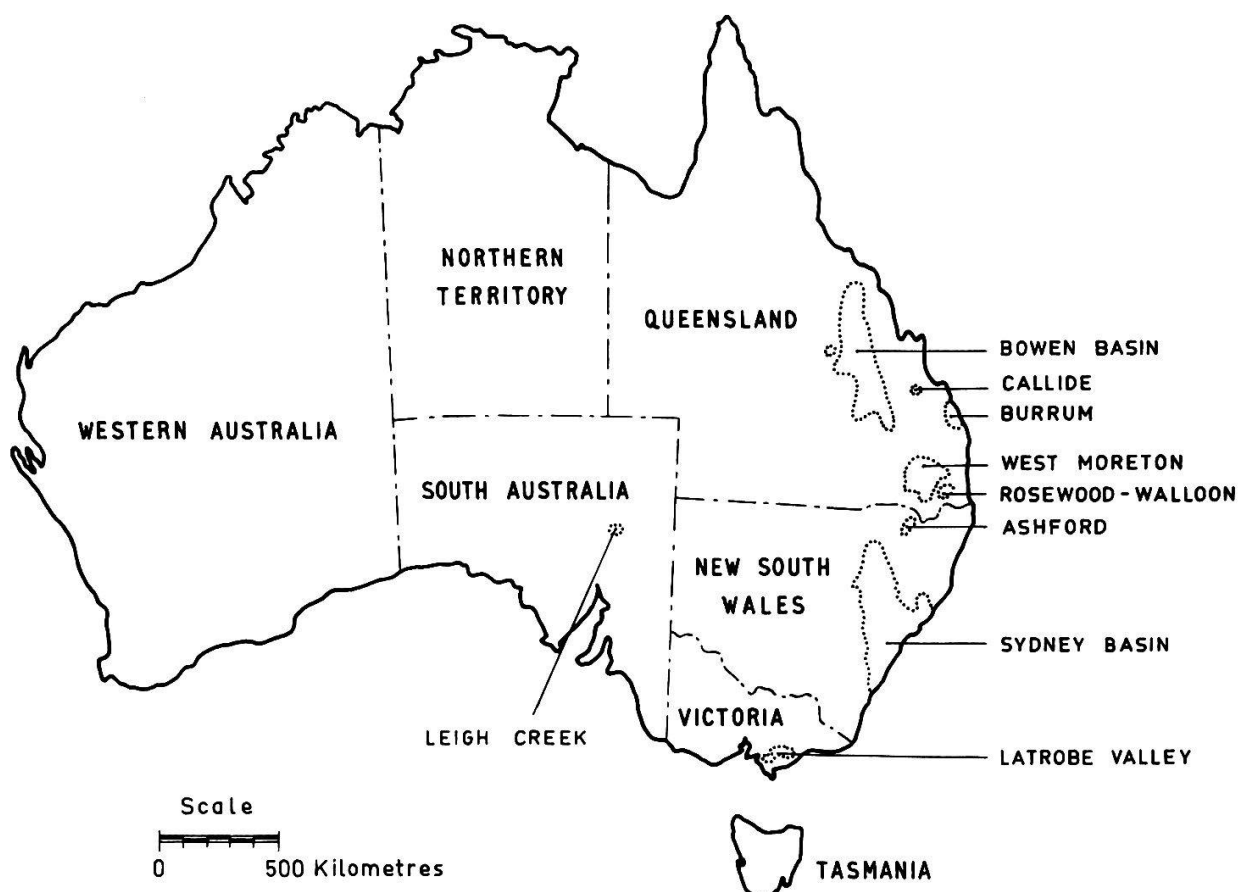


Fig. 1 Location of coalfields discussed in the text.

¹ Division of Coal Research, CSIRO, Sydney, Australia.

² Sitzung der Naturforschenden Gesellschaft in Bern vom 21. September 1965.

From the practical point of view it has been found useful to regard as coal any sample having an ash yield of less than 35 % at 800 °C, under standard conditions. The bituminous (i. e. hard) coals of Queensland and New South Wales are of variable ash yield (mostly in the range 5—25 %). They are usually low in sulphur (i. e. less than 1.3 %) and very low in chlorine (about 0.01 %), while phosphorus tends to be above 0.02 %. The Victorian brown coals, which are being mined by open-cut methods in the Latrobe Valley, have low ash yields (less than 5 %), and are low in sulphur and very low in phosphorus (less than 0.01 %). However, chlorine is variable and may be as high as 0.3 %. The Leigh Creek coals (hard brown) from South Australia are very variable in ash yield (7.5-32 %, with a mean of about 20 %) and usually high in sulphur, chlorine and phosphorus. Australian coals range from Permian (most of the hard coals) to Tertiary (Victorian brown coals) and the seams tend to be thicker than ordinarily found in Europe. For example, seams of 2-4 m are common in New South Wales; the 30 m seam at Blair Athol in Queensland is exceptional. In parts of the Latrobe Valley the brown coal deposit exceeds 100 m in thickness.

In accordance with the modern trend, Australian power stations are situated on or near coalfields. This has the advantage that long-distance transport of coal is avoided. Also, modern coal-winning equipment is used for mechanical mining underground and for open-cut operations. For example, a dredger on the Latrobe Valley coalfield may have an output of up to 1500 metric tons per hour. An additional advantage of this «on site» power generation is that there is less likelihood of trouble from atmospheric pollution, as these power stations are at present fairly remote from the main centres of population. However, this is not a solution to the overall problem of air pollution.

Coal usage in Australia derives its main impetus from the demand for energy, which is increasing at an average annual rate of about 10 % and which comes mainly from coal. Hydro-power and oil are secondary to coal; they account for less than 20 % of the total energy produced, while natural gas and atomic energy have yet to be used in Australia.

II. Composition of Coal, and Mode of Occurrence of Inorganic Constituents

The ranges of contents for the main inorganic constituents in ashes derived from hard, brown, and hard brown coals from three important sources are given in Table 1. The compositions of most Australian coal ashes would fall within these ranges (BROWN, CLARK and DURIE, 1959). In general, the hard coals yield ashes high in silicon and aluminium, with iron and calcium high when sulphide and carbonate minerals are present in more than normal amounts. The ashes from brown coals are high in iron, calcium, magnesium, sodium and sulphur; phosphorus being very low. In keeping with their name, hard brown coals tend to give values intermediate between those for hard coal and for brown coal.

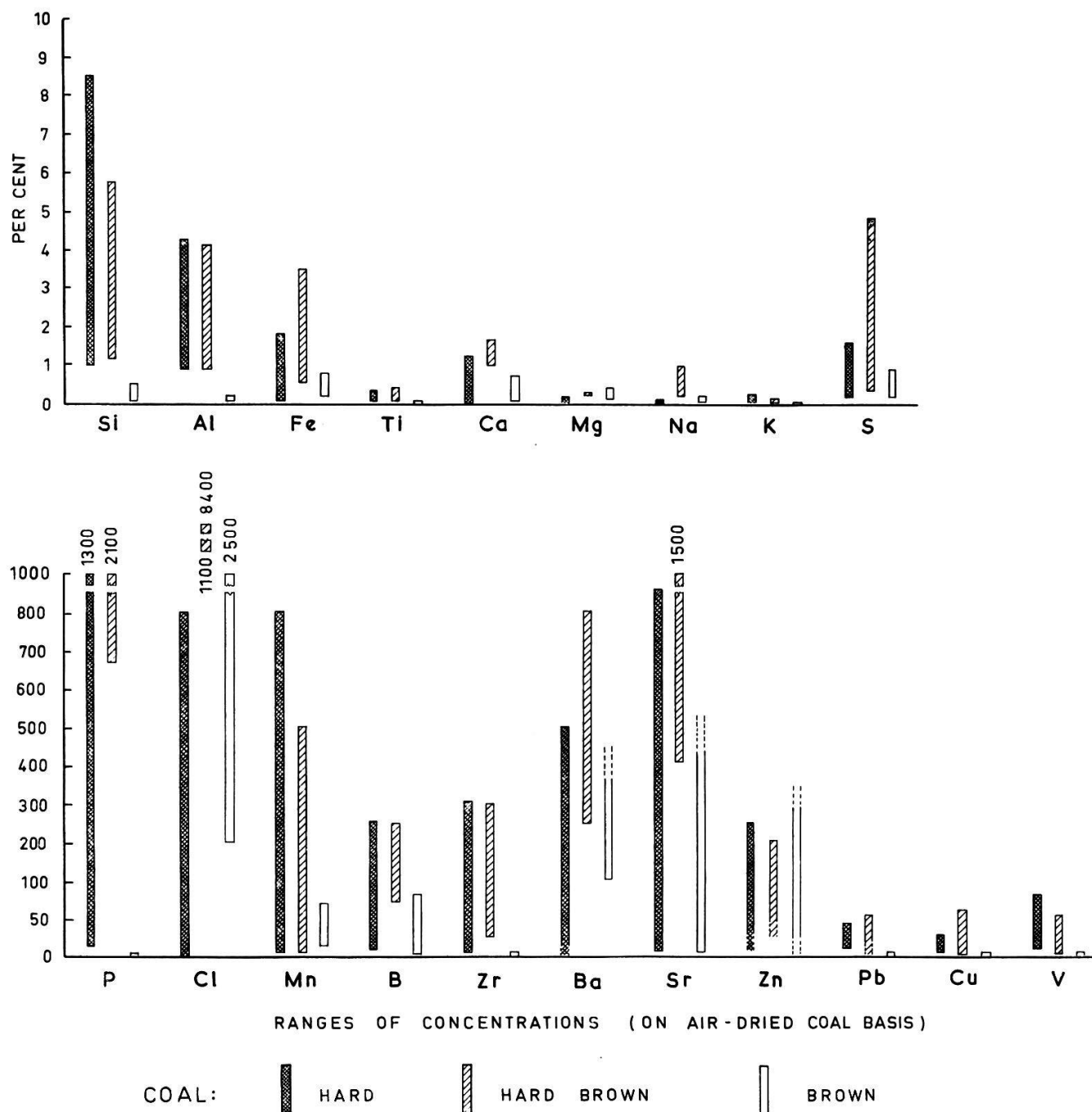


Fig. 2 Inorganic Constituents in Australian Coals.

Although a consideration of the composition of coal ash is useful from a practical point of view, mainly in connection with slags, it is also useful to cite the contents of inorganic constituents in terms of the element in the original coal. On an air-dried coal basis, the ranges of concentrations of 33 inorganic constituents in Australian hard, hard brown, and brown coals are shown in Figs. 2 and 3. These ranges are for 90 % of samples examined (CLARK and SWAINE, 1962).

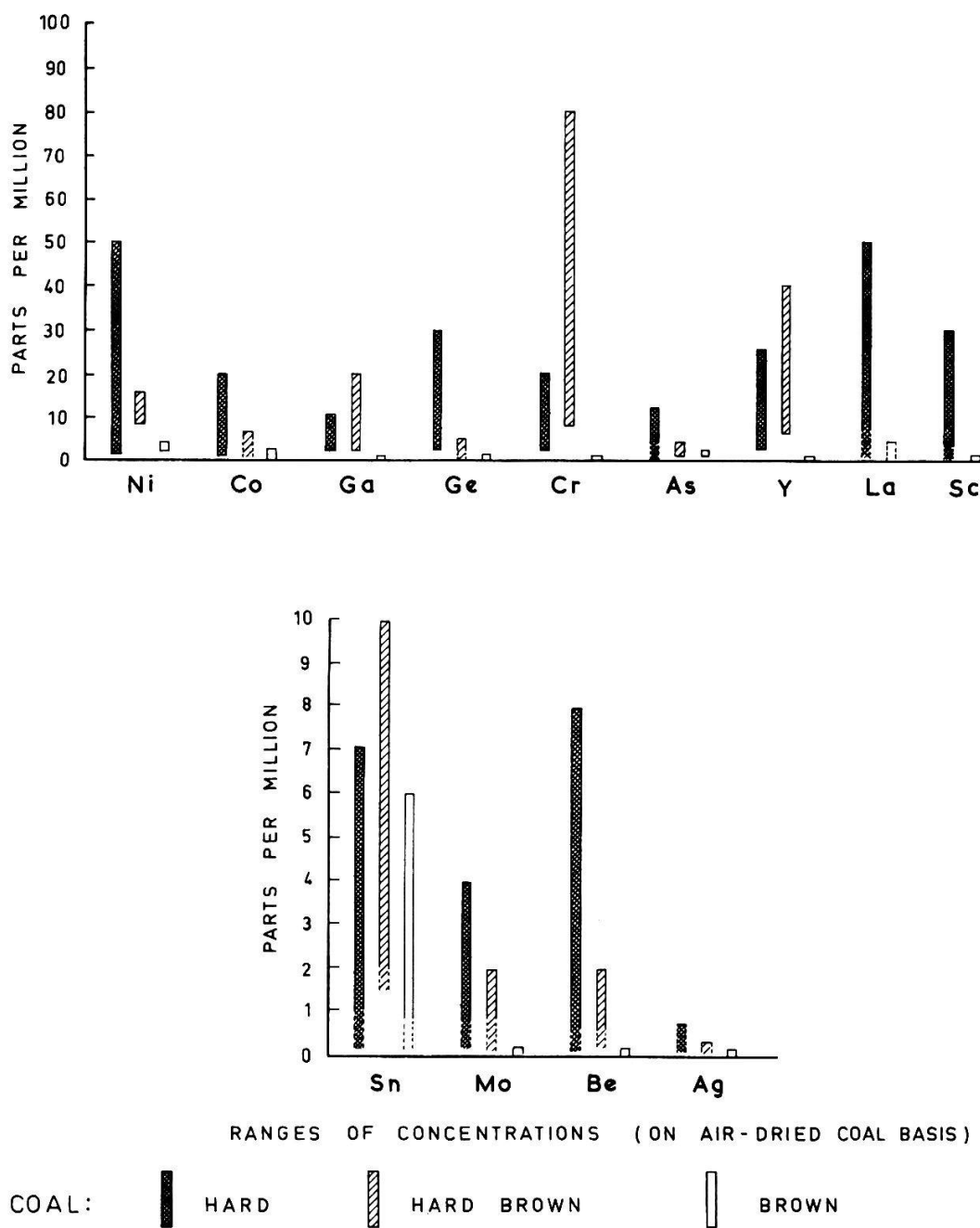


Fig. 3 Inorganic Constituents in Australian Coals.

Inorganic constituents may occur in more than one form, namely associated with specific minerals, as minor replacement cations in minerals, and associated with the organic coal substance. Variations in the concentrations of the different elements in Australian coals are shown clearly in Figs. 2 and 3 (based on BROWN and SWAINE, 1964). The reasons for these variations have been ascertained in many cases. As a result of the examination of many coals by various methods

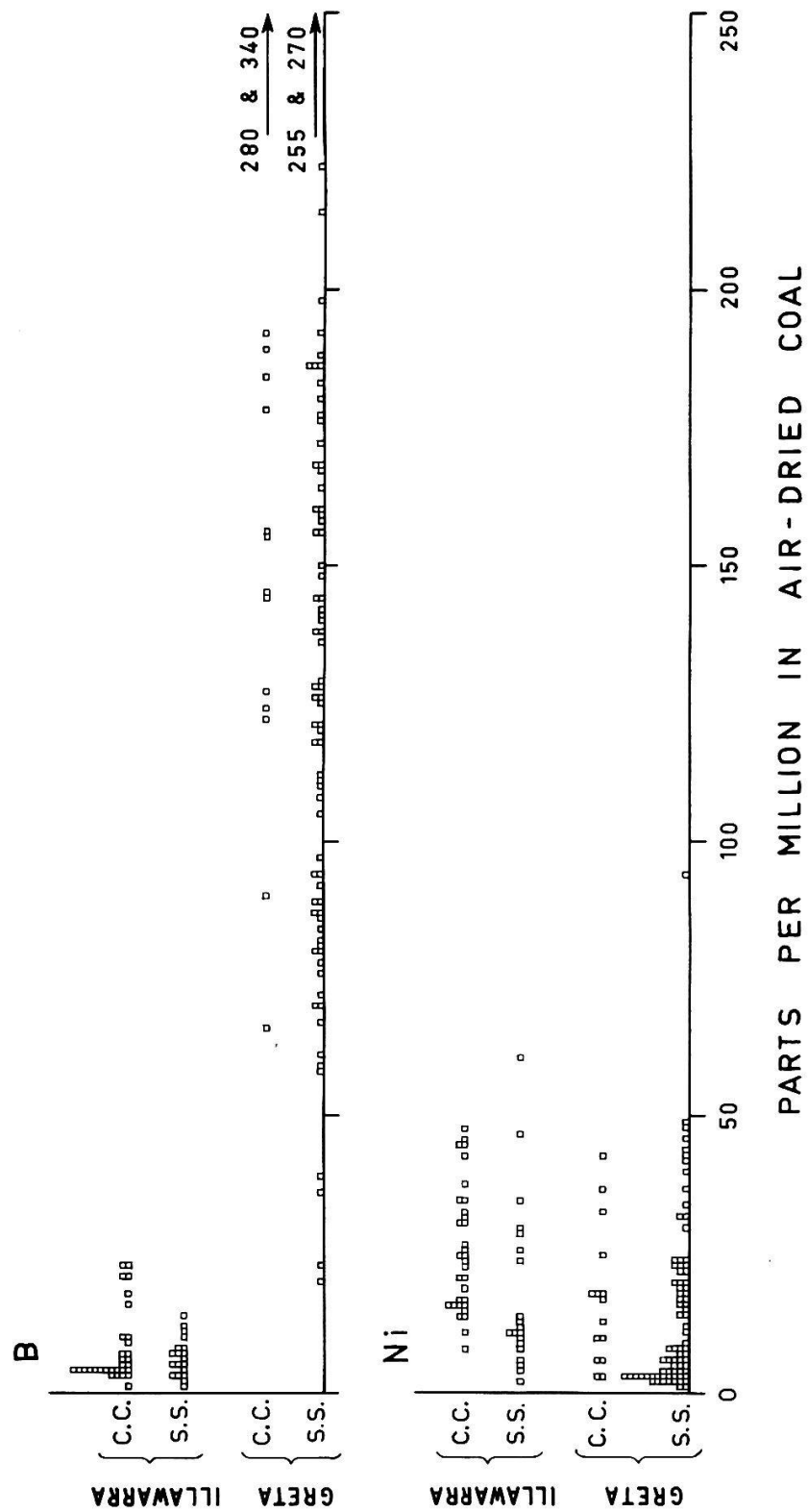
a good deal is known about the mode of occurrence of several elements in Australian coals (TAYLOR and WARNE, 1960; KEMEZYS and TAYLOR, 1964). Silicon is found in clays, silicates and free quartz, and aluminium in clays. Iron occurs in pyrite, marcasite and siderite.

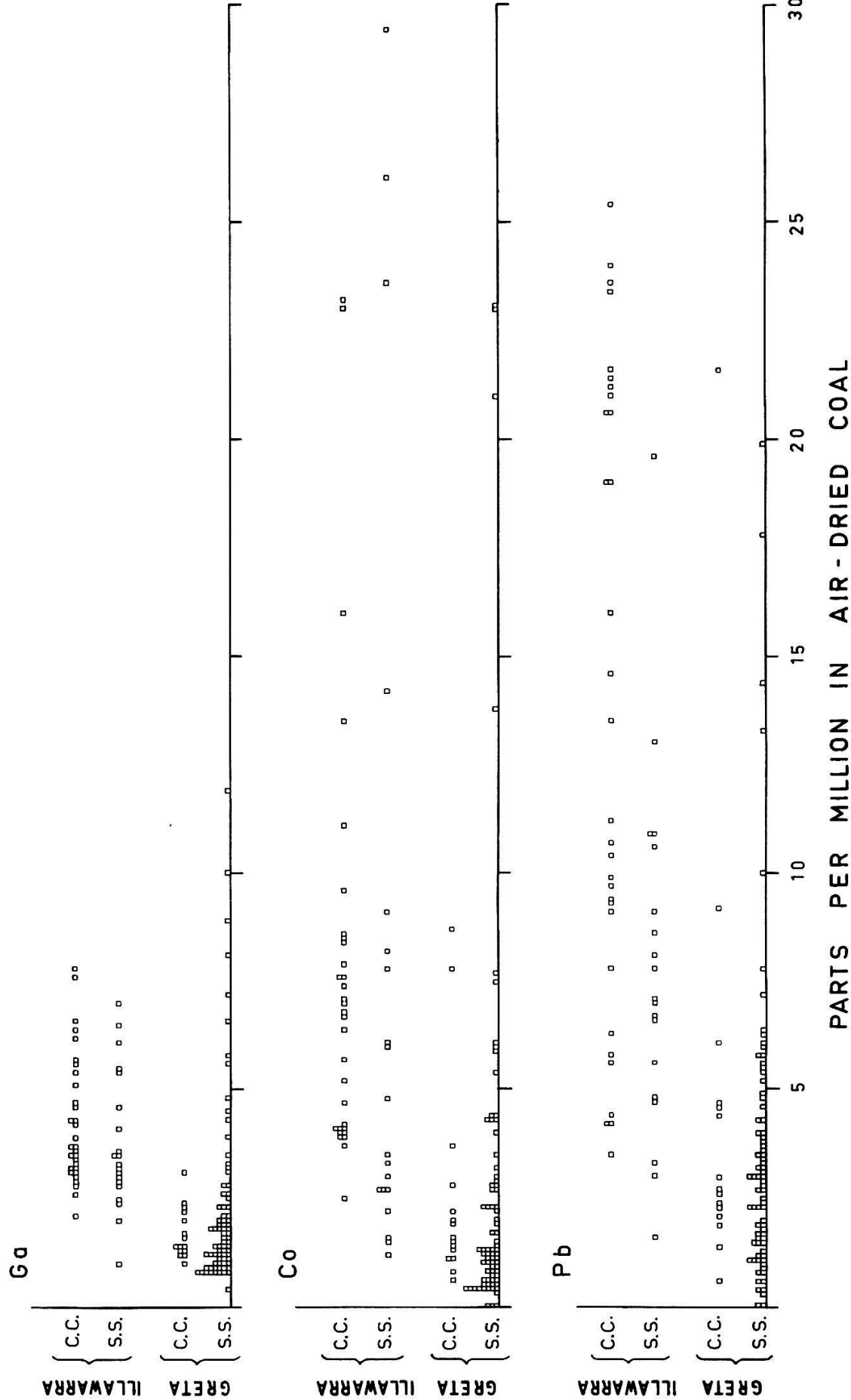
Titanium has been found in mineral form, and there is every possibility of Australian coals containing organically bound titanium. Carbonates are the main mineral form of calcium, magnesium being usually only a minor constituent of carbonates. Calcium also occurs as gypsum, and magnesium occurs in some clays. It may be deduced from the generally low chlorine content of Australian hard coals that sodium and potassium cannot be present only as chlorides. Sodium may occur in certain clay minerals and feldspars, and potassium in some aluminosilicates.

It has been shown that the brown coals contain organically bound calcium, magnesium, iron, sodium and (to a lesser extent) potassium (DURIE, 1961); these cations partly replace hydrogen in carboxyl groups ($-\text{COOH}$) in the coal, giving rise to coals with varying amounts of free carboxyl and of metal carboxylates (DURIE and SCHAFER, 1965). Most of the sulphur is present in mineral form (as pyrite and marcasite) and organically bound; some other sulphide minerals are minor constituents of certain coals. Although gypsum is found in some coals — for example, those from Leigh Creek — the concentration of sulphate sulphur is usually low (less than 0.05 % expressed as S). Manganese has been found in siderite and calcite (up to 1 % Mn), and may occur organically bound in some brown coals.

Amongst other minerals which have been found in Australian coals are fluorapatite, barite, sphalerite, galena, chalcopyrite, millerite and zircon. The traces of strontium which have been found in samples of calcite, barite and gypsum, separated from certain coals, are insufficient to account for the high concentrations of strontium in some brown and hard brown coals, where it would seem likely that some organically bound strontium is present. An extensive investigation of about 500 samples showed that scandium varied from less than 0.05 part per million (p.p.m.) in brown coals to 30 p.p.m. in a Queensland hard coal (SWAINE, 1964). The mean content for most N.S.W. and Queensland hard coals was 2.5-3 parts per million of scandium, but Triassic coals from the West Moreton coalfield (Fig. 1) had a mean Sc content of 15 p.p.m. Minerals associated with hard coals were analysed spectrographically for scandium, with the following results: less than 20 p.p.m. in pyrite, up to 10 p.p.m. in calcite, up to 25 p.p.m. in kaolinite and up to 40 p.p.m. in siderite. No specific scandium minerals have been found in Australian coals or associated dirt bands, but the examination of coal samples, which had been treated chemically to reduce the ash yield to $\approx 1\%$ or less, indicated that between 40 % and 90 % of the scandium in some coals is organically bound to the coal substance. Unlike gallium, germanium, lead, and some other trace elements, scandium is not enriched in deposits on the superheaters and screen tubes of boilers burning Australian coals.

Fig. 4 Concentrations of Boron, Nickel, Gallium, Cobalt and Lead in Coals influenced by Freshwater and Marine Conditions.





ILLAWARRA (FRESHWATER - INFLUENCED)
GRETA (MARINE - INFLUENCED)

C.C. - CLEAN COAL COMPOSITES
S.S. - COAL SUBSECTION SAMPLES

In most Australian coals arsenic seems to be associated with pyrite, possibly as arsenopyrite, but there is as yet no evidence for the mode of occurrence of boron, vanadium, cobalt, gallium, germanium, chromium, yttrium, lanthanum, tin, molybdenum, beryllium or silver.

III. Trace Elements in Coal as Environmental Indicators

It does not seem unreasonable to expect that the concentrations of some trace elements in coal would differ according to the environmental conditions to which the coal had been subjected. Earlier work had indicated that low concentrations of boron were a feature of coals from the Illawarra Coal Measures which had been subjected only to post-depositional freshwater conditions, whereas higher concentrations were found in Greta coals which had been affected by subsequent marine conditions. These are Permian coals from the Sydney Basin (Fig. 1). On the basis of these concentrations it was suggested that the Tomago Coal Measures had been influenced by intermittent marine or by brackish conditions (SWAINE, 1962). Further evidence of this possibility has been put forward by DIESSEL (1965); as a result of a study of tonsteins he suggested that some coal seams in the Newcastle area may have been formed in estuaries. The possibility that other trace elements may be useful as indicators of marine or freshwater influences on coals has been examined. On the basis of samples from the Illawarra and Greta Coal Measures, sufficient differences were found in the levels of nickel, gallium, cobalt and lead for these elements to be useful environmental indicators. Some results for these elements, as well as for boron, are shown in Fig. 4; a clean coal composite is a representative sample of a seam prepared from all subsections with ash yields of less than 35 %. Gallium and cobalt and, to a lesser extent, nickel and lead, tend to occur in higher concentrations in the Illawarra coals (freshwater-influenced) compared with the Greta coals (marine-influenced). If sufficient samples are considered then these five elements should indicate the environmental conditions to which a coal from the Sydney Basin has been subjected, the level of confidence being greater than when boron only is used.

On the basis of the results in Fig. 4 for marine- and freshwater-influenced coals, and designating intermediate values as brackish, an assessment was made of the Tomago Coal Measures; 35 samples, comprising 7 clean coal composites and 28 coal subsection samples, were analysed. 90 % of the results indicated that marine or brackish influences had affected these seams. Whether or not these elements are also useful indicators of environmental conditions which have affected other Australian coals has not yet been established. Perhaps regional effects could vitiate the general applicability of these elements or perhaps the relevant concentration ranges would be different for other coal measures. It is interesting that the mean boron content of sediments associated with coals in the Sydney Basin (dirt bands, roof and floor subsections) is 85 p.p.m. boron, which is the

same as the mean content for sediments as cited by HARDER (1963). At present the mode of occurrence of boron, gallium and cobalt in Australian coals is not known, although there is indirect evidence that boron is organically bound, at least in part. A knowledge of how these elements occur in coals would aid the interpretation of trace-element data in relation to environmental effects.

IV. Methods Used for Investigating Inorganic Constituents

A wide range of techniques is used in the investigation of the inorganic constituents in Australian coals. Coal ash is analysed for its major constituents by rapid methods, based mainly on flame photometry and spectrophotometry (DURIE, SCHAFER and SWAINE, 1965). Calcium, magnesium, sodium, potassium and iron, extracted from brown coals by dilute hydrochloric acid, are determined by atomic absorption spectrometric methods (DURIE, SCHAFER and SWAINE, 1963). Silicon, aluminium, iron, calcium, potassium, titanium, sulphur and chlorine are determined directly on low-ash brown coals by X-ray emission spectroscopic techniques (SWEATMAN, NORRISH and DURIE, 1963). Sulphur can be determined directly in fly-ash by X-ray emission (GOADBY and STEPHENS, 1967), and further work is in progress to extend this technique to coals generally for a wider range of elements. Trace elements are estimated by atomic emission spectrographic methods, using powdered coal ash in a direct-current arc. A general semiquantitative spectrographic method has been developed for use when only a small amount of sample is available. In this method, 1-2 mg of sample is buffered with lithium tetraborate and graphite, and the mixture is filled into a graphite electrode, which is used as anode in a 9-ampere direct-current arc.

The inorganic composition of minute mineral grains in coals is determined by using a ruby laser to vaporize about a microgram of the sample. The general arrangement of the laser used for this purpose, known as the laser microprobe, is shown in Fig.5. The laser beam is deflected by a right-angle prism down through an optical microscope (the viewing mirror having been moved out of the vertical light path) and is brought to a focus on the sample by the microscope objective. Two graphite spark electrodes are positioned 1-2 mm above the sample.

An analysis is carried out by selecting the required area of specimen under the microscope, and then firing the laser. The vapour of the sample rises between the spark electrodes, which have been charged to about 1.5 kV, thereby discharging the spark-gap. The resulting radiation, focused sharply on the slit of a spectrograph, gives a spark-like spectrum, from which the elements in the sample can be identified. A Q-switched laser is used and the sample is vaporized without sputtering or initial formation of a liquid. This phenomenon, which cannot be simply explained in terms of classical thermal theory, may depend — at least partly — on the shock wave associated with the laser pulse.

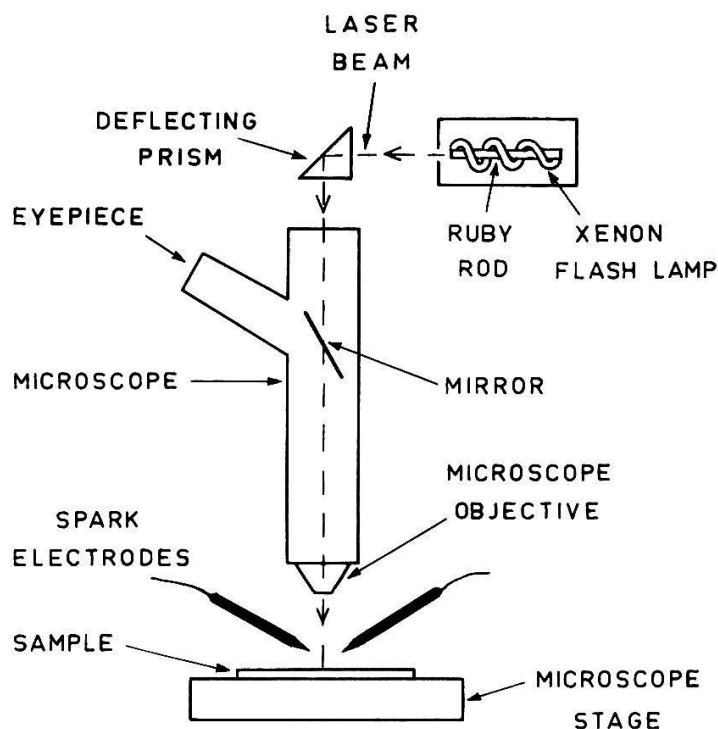


Fig. 5 Laser and microscope arranged for vaporization of micro amounts of material.

Amongst the other techniques used for investigation of inorganic constituents and minerals at the Division of Coal Research are X-ray diffraction, infrared spectrometry, optical microscopy, electron microscopy and diffraction and differential thermal analysis.

V. Practical Importance of Inorganic Constituents

Efficient utilization of coal cannot be achieved without a knowledge of the nature and function of the inorganic constituents. Under the combustion conditions used for power generation the inorganic constituents contribute to the formation of slag, deposits on the fireside surfaces of the superheater and other parts of the boiler, and also fly-ash. For example, under certain conditions, when using spreader stokers or chain-grate stokers, hard coal may give rise to dense, firmly adhering deposits on the fire side of superheaters and other parts of the boiler. These deposits have much higher concentrations of some elements than the coal being burnt. In Fig. 6 results are presented for the outer and inner layers of a deposit on the wall of a superheater tube. Relevant values for the hard coal (on an ash basis) which was being fired are also given, for purposes of comparison. The inner phosphatic layer, which is about 0.5 mm thick, shows an enhancement of arsenic, boron, thallium and other volatile elements, but not of vanadium, yttrium and similar refractory elements. In this case boron phosphate (BPO_4)

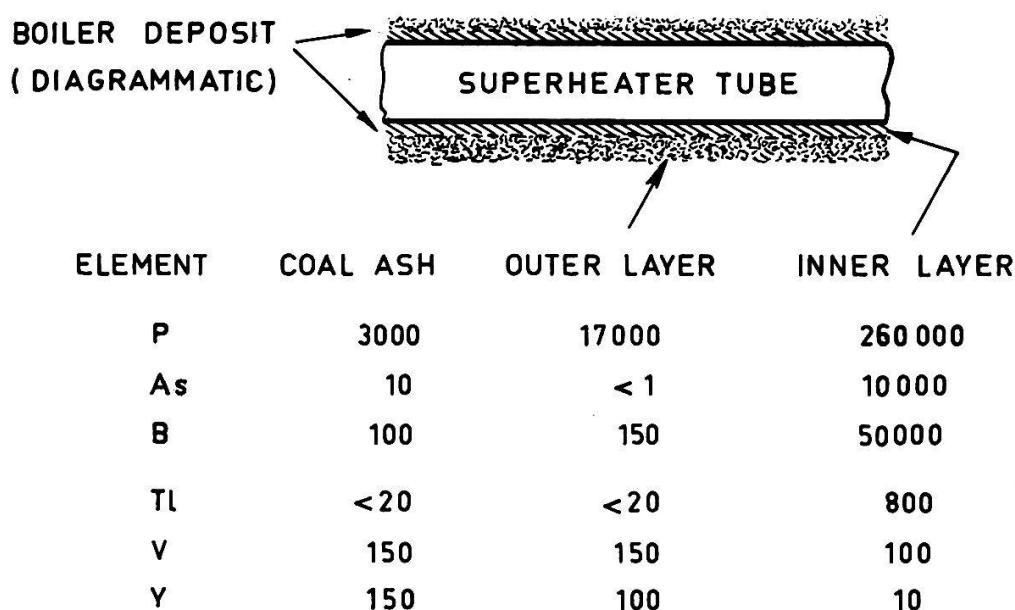


Fig. 6 Concentration variations of some Inorganic Constituents in a boiler deposit.
(Values are in parts per million)

was identified in the inner layer. This compound of high melting point formed a hard, tightly adhering layer on the metal tube and reduced the efficiency of heat transfer from the hot gases to the fluid inside the superheater tube. The high concentration of arsenic in the inner layer of the deposit compared with the coal is noteworthy, and it is possible that boron arsenate (BAsO_4) may have been formed, as it is isostructural with boron phosphate. Thallium has not been detected in Australian coals, which means that it is not present at more than the 1-2 p.p.m. level, but it has been found concentrated in the inner layers of some phosphatic boiler deposits.

In modern methods of pulverized-fuel firing, these phosphatic deposits have not been found. However, the combustion of brown and hard brown coals has given rise to another type of deposit, characterized by high concentrations of alkali and alkaline earth sulphates. Although the composition of these deposits is known, further work is required to ascertain how they form, and the conditions in the boiler that are most relevant to their formation. In the early stages of combustion of these brown coals a thin film appears on superheater and other heat-transfer surfaces. This film is mainly sodium chloride or sodium sulphate, and as the film builds up the heat transfer through the tube wall is impaired. This in turn causes an increase in temperature of the deposit. Then either the components may melt or a sodium chloride — sodium sulphate eutectic may form which has a lower melting point than either of its components. The resultant sticky surface assists the adhesion of residual inorganic material from the coal (fly-ash), and secondary reactions may then give rise to the formation of calcium sulphate, which binds the boiler deposit into a compact mass.

It is evident that boiler deposits decrease the efficiency of the heat transfer from the hot combustion gases to the metal boiler tubes, and hence they are a major factor in the overall inefficiency of power stations. It is for this reason that research is being carried out on all aspects of boiler deposits, with the aim of alleviating their effect or preventing their formation.

VI. Concluding Remarks

From the foregoing it is clear that the inorganic constituents are of prime importance in the utilization of Australian coals, especially for power generation. In other branches of coal science also — for example, in geological studies of coal measures — knowledge of the inorganic constituents of coal is necessary. Hence, research is continuing on a wide range of aspects of this subject.

For the privilege of addressing the Naturforschende Gesellschaft I thank your President and Council. I am grateful to Mr. H. R. Brown, Chief of the Division of Coal Research, CSIRO, for his encouragement. The several members of the staff of the Division whose work is embodied in this paper are mentioned in the list of references.

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Table 1 Percentage Composition of Coal Ash (Range of Values)

	Hard Coal (Sydney Basin)	Brown Coal (Latrobe Valley)	Hard Brown Coal (Leigh Creek)
SiO ₂	45—63	3.5—34	16—49
Al ₂ O ₃	22—37	2—20	13—27
Fe ₂ O ₃	0.5—15	5.5—42	5—32
TiO ₂	0.6—2	0.1—2	0.8—2.5
CaO	0.0—5	9—52	4—18
MgO	0.0—3	7—21	1—6
Na ₂ O	0.0—1.5	0.8—10	1—12
K ₂ O	0.0—2	0.0—1	0.1—1.5
P ₂ O ₅	0.0—2	0.01—0.2	0.3—3
SO ₃	0.2—3	12—29	4.5—17