THE AAPIESBOOMEN MAGNESITE DEPOSIT, BURGERSFORT, TRANSVAAL

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list of illustrations and tables

abstract

The published literature on magnesite is extensively reviewed as regards the properties, uses, production, occurrence and genesis of the mineral.

The structure of magnesite is assumed to be the same as that of calcite, which in turn consists of a face-centred rhombohedral cell. Pure magnesite is composed of $MgCO_3$, but complete solid solution has been demonstrated between $MgCO_3$ and $FeCO_3$ and between $MgCO_3$ and $MnCO_3$. Substitution of Ca, Ni, Co and Zn for Mg also occurs to a limited extent. The mineral is optically negative with refractive indices that vary between 1,509 and 1,563 for E and 1,700 and 1,782 for W, depending on the nature and degree of cation substitution. Magnesite occurs in two characteristic forms : cryptocrystalline or gel magnesite and the crystalline or spathic variety. Both are usually white in colour and have a hardness of 3,5-5 and a S.G. of 3,0-3,2. The thermogram exhibits a single large asymmetric endothermal peak which lies between 650 and 700°C.

Despite opposition from the producers of sea water magnesia in recent years, magnesite still finds a ready market for the manufacture of refractory materials, particularly in the steel industry. Less important uses include the manufacture of magnesium metal, carbonic acid gas, Sorel cement, paper, pharmaceuticals and fertilizers.

Large bodies of cryptocrystalline magnesite occur in Greece,

.........../Yugoslavia ......

Yugoslavia, Turkey and India, while the deposits in Austria, Czechoslovakia, Russia and China produce most of the world supply of crystalline material.

Four types of magnesite bodies may be distinguished : quartz-magnesite deposits, talc-magnesite occurrences, magnesite associated with sedimentary rocks and sagvandite, a magnesite-bronzite rock. Most South African deposits, including the Aapiesboomen body, belong to the first type. Experimental, field and textural evidence indicates that the quartz-magnesite deposits may form from serpentine under a wide range of hydrothermal and supergene conditions below about 400°C and between very low and very high concentrations of CO_2 in the fluid phase. Above 400°C talc is produced at the expense of quartz. Sedimentary magnesite has been observed to form in present day saline lakes, but the large size of the older crystalline deposits associated with limestones and dolomites has been used as an argument against the use of the same principle to explain the genesis of the latter bodies : much controversy still surrounds the sedimentary-hydrothermal debate concerning their origin. It seems probable that sagvandites are produced by a process of CO_2- metasomatism.

One of the hydrated carbonates (usually hydromagnesite or nesquehonite) invariably forms in preference to magnesite under conditions of low temperature and pressure, both in the laboratory and in nature. The reluctance of magnesite to crystallize directly from solution has been attributed to the strong hydration of the Mg^{2+} ion.

The Aapiesboomen deposit occurs as an elongate shallow blanket-like body situated on a flat plain between the

........../Hoosi .....

Hoosi river and a range of hills approximately 6 km west of Burgersfort on the main Lydenburg-Pietersburg road. The hills are composed of alternating bands of basal norite and pyroxenite of the Bushveld Igneous Complex : peridotites are confined to the lowermost slopes.

The peridotites and pyroxenites situated on the lower hill-slopes have been extensively altered to quartz and carbonate and accessory phlogopite. In addition, the peridotites contain serpentine, hornblende and minor brugnatellite. Irregular and regular carbonate veins ranging in thickness from 1 mm to 10 cm commonly traverse the altered parent rocks. The carbonate comprising the veins is dominantly magnesite, with lesser amounts of dolomite, while in the altered peridotites and pyroxenites this ratio is reversed. Textural evidence indicates that in the peridotites the alteration process was initiated by the serpentinization of the olivine, closely followed by saussuritization of the feldspar and then the formation of quartz and carbonate and later of hornblende, brugnatellite and phlogopite. Only the early stages in the alteration of the pyroxenites were studied : this revealed saussuritization of the feldspar and the formation of quartz, carbonate and phlogopite at the expense of pyroxene.

Chemical analyses of seventeen altered and unaltered host rock specimens were recalculated to obtain the number of cations associated with 100 oxygens and assuming isovolumetric change, the following chemical variations accompanying the progressive alteration of the rocks deduced : loss of Si and small amounts of Al, Mg, Fe^{3+} and Na; increase of C; initial increase of OH followed by decrease; oxidation of Fe^{2+}; and a slight increase in Ca.

It is postulated that the changes were effected by surface

.........../ weathering ......

weathering processes.

The blanket-like massive magnesite deposit occurs on the surface and nowhere does the thickness exceed 8 m. Rounded pebbles and boulders of pyroxenite are scattered throughout the thickness of the body and it seems most probable that the deposit was formed by the precipitation on the flat plain of magnesite derived from the weathering of the basic and ultrabasic rocks on the hill-slopes and transported downslope in solution. Impurities in the massive ore are quartz, dolomite, palygorskite, magnetite and chromite, all of which are concentrated in pockets between the semi-consolidated magnesite nodules, which vary in size from a few cm to approximately 1 m. Significant quantities of impure material also occur finely disseminated throughout the nodules. The estimate of 5,5 million tons made by Goldfields of S.A. Ltd. on the basis of extensive wagon drilling is considered to be the most reliable estimate of the ore reserves.

The massive ore is generally overlain by a layer composed of small (2 - 5 cm) unconsolidated nodules of dolomitic magnesite, which in turn is usually capped by a thinner layer of blanket reef made up of small (1 - 2 cm) irregular fragments of magnesite set in a ferruginous calcrete matrix. It is proposed that the uppermost 1 - 2 m of blanket reef and nodular ore results from the surface weathering of the massive ore during which Mg is preferentially leached by downward percolating waters and Ca concentrated at the surface.

FRONTISPIECE.

Westward-looking view of the hills which cover the southern part of Aapiesboomen. Pyroxenites of the B.I.C. stand out as prominent bands in the less resistant norites.

one

magnesite : a review

1.1. Properties of Magnesite

1.1.1. Structure

In the absence of any single-crystal structural analysis of magnesite the structure is assumed to differ from that of calcite only in the substitution of Mg for Ca and in the cell parameters. (DEER et al. 1962). BRAGG (1937) has described the structure of calcite by analogy with that of halite, with Ca^{2+} and $(CO_3)^{2-}$ ions respectively replacing the Na^+ and Cl^- ions of halite and the cubic unit cell being distorted by compression along a trial axis to yield a face-centred rhombohedral

........../cell. .....

cell. The distortion of the cube is necessary to accommodate the large planar CO_3 groups, which contain a carbon ion at the centre of an equilateral triangle of oxygen ions. Since successive CO_3 triangles along the rhomb edge point in opposite directions, a true face-centred rhombohedral cell contains 32 $CaCO_3$. The lattice can, however, be fully described by a smaller rhombohedral cell containing 2 $CaCO_3$ and Z is thus taken as 2. The space group of magnesite is $R\bar{3}C$.

1.1.2. Chemistry

The chemical formula of magnesite is $MgCO_3$ and when pure it contains 47,6% MgO and 52,4% CO_2. Fe^{2+} and Ca^{2+} commonly substitute for Mg^{2+}; less common replacements are Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} for Mg^{2+}.

Investigations by ROSENBERG (1963) and GOLDSMITH et al. (1962) show complete solid solution between $MgCO_3$ and $FeCO_3$ down to 295°C. Rosenberg (op.cit.) found a linear increase in the d_{211} spacings with increasing $FeCO_3$ content. Carbonates intermediate in composition between magnesite and siderite are common in nature; Breunnerite is the name given to the ferroan variety of magnesite which extends from 5 to 50 mole per cent $FeCO_3$.

JOHANNES (1968) has demonstrated the influence of temperature on the composition of the carbonate in the system $Mg^{2+}- Fe^{2+}- CO_3^{2-}- Cl_2^{2-}- H_2O$. He found that at high temperatures solid solutions rich in $MgCO_3$ are formed,

........../ and .....

and at lower temperatures $FeCO_3$-rich carbonates are produced. Thus at 200°C a Mg-rich solution is in equilibrium with a Fe-rich carbonate, while at temperatures above 350°C a Fe-rich solution coexists with a Mg-rich solid phase.

The subsolidus phase relations down to 500°C in the system $CaCO_3$-$MgCO_3$ have been studied by HARKER and TUTTLE (1955) and by GOLDSMITH and HEARD (1961) at CO_2 pressures high enough to prevent the decomposition of the carbonates. The solubilities of both $MgCO_3$ in dolomite and $CaCO_3$ in magnesite are very low. The solubility of magnesite in dolomite is about 5 mole per cent at 1200°C, 2½% at 1100°C and less than 1% between 500° and 900°C. HARKER and TUTTLE (op.cit.) could not detect any $CaCO_3$ in magnesite at 500°C, and found only ½ weight per cent at 600°, 1% at 700°, 1½% at 820° and 2% at 900°C. GOLDSMITH and HEARD (op.cit.) found 3½ mole per cent at 950°C and approximately the same amount at higher temperatures. Thus, at moderate and low temperatures the dolomite and magnesite in equilibrium are both essentially pure compounds. GOLDSMITH and GRAF (1958) report a linear increase in <u>a</u>, <u>c</u> and d_{211} with increasing $CaCO_3$ content.

GOLDSMITH and GRAF (1960) found complete miscibility between magnesite and rhodochrosite down to 500°C. Below this temperature reaction was incomplete, although no evidence for the existence of an equilibrium two-phase assemblage could be detected. These authors inferred a linear variation in the d_{211} spacings between 2.740 A for magnesite and 2.845 A for rhodochrosite.

GOLDSMITH (1972) succeeded in synthesizing Cd-rich

........../magnesites .....

magnesites at temperatures as low as 650°C, although no such naturally occurring substitution has been recorded.

Complete solid solution between $CoCO_3$ and $MgCO_3$ and a small solubility of $NiCO_3$ in $MgCO_3$ have been reported down to 600°C at 15 kb pressure. (GOLDSMITH and NORTHROP, 1964).

The substitutions are all explicable in terms of ionic radii. For example, the percentage difference between the size of the Ca^{2+} (0,99 Å) and Mg^{2+} (0,66 Å) ions is 50%, while the difference between Fe^{2+} (0,74 Å) and Mg^{2+} is only 12%. Thus, the substitution of Fe for Mg imposes little strain on the lattice, but incorporation of Ca into the magnesite structure requires too great a distortion for more than a few mole per cent $CaCO_3$ to be tolerated in solid solution.

1.1.3. Optical Properties

Magnesite is uniaxial and optically negative with extreme birefringence (0.191 - 0.219). The refractive indices vary as follows :

E = 1.509 - 1.563
W = 1.700 - 1.782

The substitution of Fe, Mn, Zn and Co for Mg cause a linear increase in the refractive indices and birefringence. DEER et al. (1962) and WOLF et al. (1967) have published diagrams showing the variation of the optical properties with composition for the rhombohedral carbonates.

........../When .....

When viewed with the naked eye, magnesite is white or colourless, but the iron-bearing varieties may show yellow or brown colouration. All species are colourless in thin section. A perfect cleavage on $\{10\bar{1}\,1\}$ is displayed and translation gliding may occur on $\{0001\}$ in the direction of $10\bar{1}\,1$ (DEER et al. op.cit.).

1.1.4. Physical Properties

Magnesite occurs in two distinct forms : cryptocrystalline or gel magnesite and crystalline or spathic magnesite (VAN ZYL, et al. 1942). The cryptocrystalline variety is porcellanous, dead white in colour when pure and breaks with a conchoidal fracture. It is generally purer than the crystalline type. Spathic magnesite resembles coarse-grained marble in appearance, consisting of a mass of rhombohedral crystals with distinct cleavage planes. This variety is generally not as pure as cryptocrystalline magnesite, a partial replacement of $MgCO_3$ by $FeCO_3$ being especially common. Since the presence of $FeCO_3$ facilitates sintering, crystalline magnesite is commercially more important.

Magnesite has a hardness of 3,5-5 and specific gravity of 3,0 - 3,2 (SIEGAL, 1967). The latter is increased by the addition of Fe, Mn, Co or Zn, rising to 3,50 for bruennerite containing 50 mole per cent $FeCO_3$ (DEER et al. 1962).

1.1.5. Thermal Properties

HARKER and TUTTLE (1955) determined the univariant pressure (CO_2)- temperature curve for the dissociation of

........../magnesite .....

magnesite up to 40,000 p.s.i. Decomposition to periclase commences at 600°C according to the reaction :

$$MgCO_3 \longrightarrow MgO + CO_2$$

HARKER (1958) showed that the equilibrium temperature for this reaction is primarily dependent on the partial pressure of CO_2.

GOLDSMITH and HEARD (1961) carried out two sets of decomposition experiments : one in which the tubes containing the magnesite were sealed, and another in which CO_2 was pumped into unsealed bombs containing the carbonate. It was found that, particularly in the lower P-T range, detectable decomposition of magnesite occurs at lower temperatures in sealed tubes than in samples open to CO_2 at the same pressure. The curve obtained for the open system is essentially parallel to the curve determined by Harker and Tuttle, but lies at significantly higher temperatures. The slope of the sealed-tube curve shows increasing deviation from both sets of open-system data at lower temperatures.

KRACEK (1963) quotes the dissociation temperature of magnesite at 1 atm CO_2 pressure as 404°C.

The thermogram of magnesite determined in air is composed of a single large asymmetric endothermal peak due to the dissociation to MgO. The peak temperature generally lies between 650° and 700°C (CUTHBERT and ROWLAND, 1947, and SCHWOB, 1950). The peak temperature for bruennerite is about 50°C higher than that for magnesite (WEBB and HEYSTEK, 1957). BANERJEE (1970) has found that the peak for some

........../micro-crystalline .....

micro-crystalline magnesites from India occurs at 670°C, and at 720°C for crystalline magnesites. WOLF et al. (1967) have noted the occurrence of small endothermic peaks at higher temperatures, which may be due to the presence of small quantities of Ca, Fe and/or Mn.

Thermogravimetric analyses of the Fe, Mg and Ca carbonates were first performed by SCHWOB (op.cit.). WOLF et al. (op.cit.) have compared the diagnostically different T.G.A. curves for magnesite, dolomite, calcite, ankerite and siderite.

1.1.6. Distinguishing Features

The rhombohedral carbonates are all very similar in many respects, but may be distinguished by optical, X-ray and thermal methods, as outlined in the preceding sections. In addition, various simple field tests may be applied.

STEVENS and CARRON (1948) suggest the use of abrasion pH values to distinguish between the common carbonates. The procedure consists of grinding a small sample of the mineral in a drop of water and measuring the pH of the suspension by means of indicator paper.

FRIEDMAN (1959) has proposed a staining scheme, whereby Fiegl's solution and Alizarine Red S are used to distinguish between aragonite, calcite, high magnesian calcite, dolomite, magnesite, gypsum and anhydrite.

........../ WARNE .....

WARNE (1962) expanded this method to include siderite, witherite, rhodochrosite, smithsonite, strontianite and cerussite.

The discussion by LOGVINENKO, et al. (1961) in relation to the identification of the carbonate minerals should, however, be borne in mind. These authors have pointed out that most information on the isomorphism of carbonates is related to binary series, whereas in fact many are polycomponent systems, such as (Fe, Ca, Mg, Mn) CO_3 and it may be necessary to employ quantitative chemical methods in addition to one or more of the above techniques for a complete characterization of the species.

1.2. Uses of Magnesite

Magnesite finds its chief use in the manufacture of refractory materials for the steel and allied industries. It is also used in the chemical, pharmaceutical and agricultural industries.

1.2.1. Refractory Material

Magnesite is one of the raw materials used in the manufacture of magnesia (MgO), one of the most important refractory substances. Magnesite is converted to magnesia by heating. This process involves the evolution of CO_2 and the final product is known as dead-burned or sintered magnesia, or β-periclase. Pure magnesite requires a temperature of at least 1700°C and prolonged heating before a satisfactorily sintered product is obtained. During the formation of β-periclase an intermediate product, α-periclase is formed at approximately 800 - 900°C; this

........../contains .....

contains about 5% CO_2 and is also known as calcined or caustic calcined magnesia. (VAN ZYL et al., 1942). Dead-burned magnesia has a melting point of 2500°C and is relatively inert chemically (BAIN, 1924).

Impurities in the magnesite have a catalytic effect on sintering and may lower the sintering temperature considerably. Thus breunnerite is sintered at 1500°C (VAN ZYL et al. op.cit.). Impurities also aid in holding together the magnesia grains, but result in a low crushing strength and a lowering of the melting point. Natural impurities such as serpentine, talc and dolomite are generally detrimental to the quality of the ore since they occur as veins or lenses and are not finely and evenly distributed throughout. Breunnerite, on the other hand, is ideal as it is contained in solid solution with the magnesite. (VAN ZYL et al.. op.cit.). Chrome ore is commonly added as a bonding agent in the manufacture of bricks used at very high temperatures, and for materials subjected to heavy wear tar-bonded bricks are used (ANONYMOUS, 1970a).

During the past decade the manufacture of magnesia by a process whereby sea water is passed over calcined, slaked dolomite has become increasingly important and at the present time this process accounts for much of the magnesia used in the manufacture of refractory materials. In addition, magnesia is extracted from natural brucite in Canada and the U.S.A. and since World War I dolomite has found increasing use as a refractory material and as a source for Mg-compounds. (CUMMINS and BICHAN, 1970). Natural magnesite still finds important uses in these

........../fields .....

fields, however, as shown by the rising demand for this material. (See Section 1.3.).

1.2.2. The Manufacture of Magnesium Metal

Magnesium metal has been extracted from fused magnesium chloride by electrolysis or by thermal reduction of dead-burned magnesia at 1300 - 1500°C. In both cases the purest raw magnesite was used as starting material. (VAN ZYL et al. op.cit.). These processes, however, were only of importance during the war years when normal supplies were restricted and today most metallic magnesium is produced by electrolysis or reduction of dolomite and sea water.

1.2.3. The Manufacture of Carbonic Acid Gas

During the heating of magnesite CO_2 is evolved in a step-wise manner during the formation of various basic carbonates at successively higher temperatures. (BRILL, 1905). In industry a calcining temperature of about 800°C is employed (VAN ZYL et al. op.cit.). Grade requirements for magnesite used for this purpose are not as rigorous as for the material used elsewhere; for example, high lime magnesite has been used in South Africa for the manufacture of CO_2.

1.2.4. Sorel Cement

This is the name given to the cement formed by a mixture of finely ground caustic calcined magnesia and a strong solution of magnesium chloride. (VAN ZYL et al.

........../op.cit.). .....

op.cit.). Magnesium oxychloride is known to be the bonding agent and consequently this material is also known as oxychloride cement.

Magnesia used for this purpose should be free of lime as lime has a greater tendency to absorb water and carbon dioxide than magnesia, thereby causing swelling.

1.2.5. Paper Industry

In the sulphite process of paper manufacture the wood is boiled with a disintegrating agent so that it breaks down into a mass of pulp which is subsequently rolled into paper. (VAN ZYL et al. op.cit.). Magnesium bisulphite, obtained from magnesite, may be used as a disintegrating agent.

1.2.6. Pharmaceutical Uses

Magnesite is the principal raw material from which magnesium salts such as epsom salts ($MgSO_4.7H_2O$) and milk of magnesia ($Mg(OH)_2$) are produced. (VAN ZYL et al. op.cit.).

1.2.7. Miscellaneous

Magnesite is also used for a wide variety of other purposes such as in the manufacture of rayon, fertilizer, rubber, chemical fluxes, pigments and paint, glass, ink and ceramics. (COMSTOCK, 1963).

........../1.3. Production .....

1.3. Production of Magnesite

The most important deposits of crystalline magnesite are mined in Austria, Czechoslovakia, the U.S.S.R., China and the U.S.A. The largest deposits of cryptocrystalline material are found in Greece, Yugoslavia and India; extensive development of cryptocrystalline magnesite in recent years was initiated largely as a result of the search for higher-grade materials in the face of stiff competition from the manufacturers of sea water magnesia (ANONYMOUS, 1970a). Figures for the world production, by country, of crude magnesite are summarised in Table I.

Unless otherwise acknowledged, the information following was obtained from ANONYMOUS, 1970b.

The oldest magnesite mine in the world occurs at Veitsch in Styria, Austria, where production commenced in 1881. Other Austrian mines are situated at Kraubath and Obersdorf in Styria and at Villach and Hochfilzen in the south-central region.

The Czechoslovakian mines, which are almost as old as those in Austria, are situated in an extensively mineralized region between Lucenec and Kosice in Slovakia.

In Yugoslavia magnesite has been mined since the early 1920s, but it was only in 1952 that large-scale production began. The mines at Kraljevo, about 180 km south of Belgrade, are the chief producers.

Rapid growth in the development of the large deposits of cryptocrystalline magnesite in Greece and Turkey has occurred since 1962. The most important mines are situated on the island of Euboea in Greece and near Eskisehir, Turkey.

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TABLE I.

World production of magnesite by country (short tons X 10^3).
+(After LEWIS and CAMMAROTA, 1969 and CHIN, 1971).

COUNTRY	1967	1968	1969	1970	1971
Austria	1692,4	1704,9	1773,0	1774,0	1715,7
Czechoslovakia	2321,5	2370,7	2400,0	3300,0	3900,0
Greece	406,7	486,1	629,1	832,4	995,1
Italy	5,0	5,5	4,4	-	-
Poland (e)	49,6	49,6	50,0	55,0	55,0
Spain (e)	121,3	250,2	116,2	114,6	115,0
U.S.S.R. (e)	3306,9	3306,9	1545,0	1569,0	1598,0
Yugoslavia	468,2	441,3	526,3	564,2	549,0
China (e)	881,8	992,1	1000,0	1100,0	1100,0
India	270,9	279,0	325,7	384,7	329,8
Iran (e)	6,6	7,2	23,1	22,0	22,0
North Korea (e)	1377,9	1377,9	1700,0	1800,0	1900,0
Pakistan	2,3	1,8	10,6	0,5	0,2
Turkey	93,7	129,8	241,4	313,9	314,0
Australia	26,5	25,9	25,9	24,8	22,0
New Zealand	0,6	0,9	0,9	0,5	0,6
Kenya	0,5	0,1	0,5	-	0,2
South Africa	88,2	65,9	53,0	92,9	86,7
Sudan	4,4	7,2	0,6	0,1	0,1
Tanzania	2,2	1,6			
Brazil	120,4	151,9	200,0	260,0	220,0
Mexico	-	-	-	9,0	8,8
TOTAL	11247,6	11656,4	10627,5	12218,4	12933,0

+Data for U.S.A., Bulgaria, Canada and Southern Rhodesia not available.

e - estimated.

A similar increase in production over the last 5 years has occurred in Spain, where the mine at Zubiri, Navarra Province plays a leading role.

Reported production of magnesite in the U.S.A. reached a peak in 1956 when 690 000 short tons was mined (BODENLOS and THAYER, 1973). Since 1963, when production was 471 000 long tons, no figures have been made available. Around the turn of the century California served as the only source, where cryptocrystalline magnesite was worked principally in the Coast Ranges and the western foothills of the Sierra Nevada (LAMEY, 1966). Recently only two deposits of any size have been mined in the U.S.A. : at Gabbas, Nevada and in Stevens County, Washington. Production at the latter ceased in 1968.

In Canada, only the mine at Kilmar, Quebec is still in operation, production at Wakefield having ceased in 1968.

Two high-grade deposits of crystalline magnesite are worked in Brazil : in the Alencar area in Ceara province and in the Eguas Range near Brumado in the Bahia region.

Most of the Indian magnesite is obtained from Salem in the state of Madras. These deposits are thought to be nearing exhaustion, however, and much attention is being given to the new discoveries in the Almora district.

Australia produces small quantities of magnesite annually, the bulk of which is obtained from the Trundle and Young Mining Divisions of New South Wales.

It is thought that Soviet Russia possesses the largest deposits of crystalline magnesite in the world. The most important deposit occurs at Satka, situated in the western Ural mountains,

........../and .....

and the recently discovered deposit at Savinsk in eastern Siberia has estimated reserves of 2000 million tons.

The very important crystalline deposits of China are found near the town of Ta-shih-chiao in Manchuria. The deposits in Kankyo province, North Korea are very similar to the Manchurian occurrences and even more prodigous in output.

The best South African deposits occur at Kaapmuiden in the Barberton district and at Burgersfort near Lydenburg, where the largest workings occur on the farm Aapiesdoorndraai.

1.4. Occurrence and Genesis of Magnesite

Many conflicting data have been published on the origin of magnesite. In this section the various deposits are accordingly classified according to their modes of occurrence; some of the most important deposits are described and the ideas concerning their origin outlined. Thereafter follow summaries of general works concerning the classification and genesis of magnesite occurrences. However, it is only after a consideration of the laboratory investigations into the stability of magnesite and the minerals commonly associated with it that an overall view can be obtained regarding the different varieties of magnesite and the possible conditions leading to their formation.

Magnesite occurs as an alteration product of magnesium-rich rocks, where it may be associated with quartz or talc, associated with various types of sediments and, together with enstatite, in an unusual rock type known as sagvandite.

1.4.1. Magnesite-quartz Deposits

Magnesite is commonly encountered in peridotites

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and serpentines, where it occupies shear or fracture zones or occurs as pockets or irregular veins and stockworks; deposits of a few tens of feet in thickness and a few square miles in area are not uncommon. The ore is typically of the low-iron, cryptocrystalline variety and is frequently associated with quartz and some lime, although the form of the latter is not well documented. Other impurities are rare. Deposits of this type have been variously ascribed to alteration of serpentine by ground water, weathering and hydrothermal processes.

In South Africa magnesite-quartz deposits have been noted in the Barberton Gold Mining District (HALL, 1918 and VAN ZYL et al. 1942), in the Sutherland Range and the Burgersfort and Marico Districts (VAN ZYL et al. op.cit. and WILKE, 1965).

1.4.1.1. Kaapmuiden

In the Barberton District the deposits occur along the north side of the Barberton Mountain land in a belt between Malelane in the east and Eureka Siding on the west. The most extensive deposits are those of Kaapmuiden which were mined from as early as 1905. The magnesite is confined to the serpentinites of the Jamestown Igneous Complex, where it occurs as veins and lenses which may be parallel or sub-parallel, but which are generally highly irregular. The veins vary in size from tiny stringers in the host rock visible only under the microscope to wall-like masses a

........../ few .....

few feet thick; nowhere is the ore known to extend to a depth exceeding 100 feet. The magnesite is cryptocrystalline, pure white in colour and strongly resembles unglazed china clay in appearance. Secondary silica is the most common contaminant, together with traces of serpentine and CaO. The average composition of lightly cobbed ore from Kaapmuiden is given in Table II.

HALL (op.cit.) attributed the origin of the magnesite to the weathering of the ultrabasic rocks by meteoric waters carrying CO_2 in solution. Two stages are involved in this process. The transformation of olivine to serpentine occurs first :-

$$\underset{\text{olivine}}{3Mg_2Fe_2Si_2O_8}+4H_2O+O_2=\underset{\text{serpentine}}{2H_4Mg_3Si_2O_9}+\underset{\text{magnetite}}{2Fe_3O_4}+2SiO_2$$

and this involves an increase in volume by 12.43%. This is followed by the alteration of serpentine :-

$$\underset{\text{serpentine}}{H_4Mg_3Si_2O_9}+3CO_2 = \underset{\text{magnesite}}{3MgCO_3}+2SiO_2+2H_2O$$

If the silica is not removed the latter reaction would result in an 18.90% volume increase. Volume considerations would argue against the ore persisting in depth because of the inhibiting effect of the weight of the overlying rocks.

VAN ZYL et al. (op.cit.) add that in the presence of excess CO_2 all the magnesium of the

........../olivine .....

TABLE II.

Chemical Analyses of Magnesite.

	SiO_2	MgO	CaO	Al_2O_3 + Fe_2O_3	Al_2O_3	Fe_2O_3	FeO	MnO	CO_2	H_2O	L.O.I.	Total
1.	9.64	37.19	4.52	2.46					40.70			
2.	8.51	38.32	3.36	2.94					40.12			
3.	6.03	42.78	1.56	1.40					45.78			
4.	4.75	44.20	tr.	0.76					47.32			
5.	2.43	45.88	0.10	0.53					50.66	0.40		100.00
6.	1.44	45.30	1.48	0.67					51.71	0.40		100.00
7.	1.88	45.37	0.89	0.45					51.01	0.40		100.00
8.	2.38	45.74	0.44		0.22	0.14	0.04				50.90	99.86
9.	1.25	46.17	0.36		0.36	0.25	o.12				51.49	100.00
10.	1.89	42.69	4.20		0.32	0.19	0.09				50.74	100.12
11.	0.41	47.16	0.03		0.23	0.12			51.88			99.88
12.	1.60	45.20	1.04		o.25	1.09			50.43			99.61
13.	0.86	46.94	0.55	0.55					51.10	-		100.00
14.	1.54	46.38	1.21	0.33					49.84	0.70		100.00
15.		44.11	0.43				3.84	0.24	51.15	0.05		99.82
16.		44.10	-				4.96	0.22	50.89	-		100.17
17.	0.45	43.82	0.97		tr.	3.65			50.44			

1 - 4 Sedimentary magnesite from California (BAIN, 1924).
5 Cobbed ore from Kaapmuiden (VAN ZYL, et al, 1942).
6 " " " Burgersfort (VAN ZYL, et al, 1942).
7 " " " Sutherland range (VAN ZYL, et al, 1942).
8 Ore from Nyala Mine, N. Transvaal (WILKE, 1965).
9 -10 " " Adieu Mine, " " (WILKE, 1965).
11 Magnesite from Mendocino Co., Calif. (HESS, 1908).
12 " " Sonoma " " (HESS, 1908).
13-14 Ore from Euboca, Greece (BOYDELL, 1921).
15 Bruenneritic magnesite from Lejarklumpen, Sweden (DU RIETZ, 1937).
16 Bruenneritic magnesite from Säkok, Sweden (DU RIETZ, 1937).
17 Spar magnesite from Grenville, Quebec (BAIN, 1924).

may pass directly into magnesite :

$$\underset{\text{olivine}}{4Mg_2Fe_2Si_2O_8}+6H_2O+8CO_2+2O_2=\underset{\text{limonite}}{2(2Fe_2O_3.3H_2O)}+\underset{\text{magnesite}}{8MgCO_3}+8SiO_2$$

These reactions involve the production of 32.2% silica and, since the average magnesite contains far less than this, it follows that much of the silica must have been removed in solution. These authors also present evidence for the transport of the ore over short distances, but conclude that most of the ore was formed by in situ alteration.

1.4.1.2. Lydenburg area

Other magnesite-quartz deposits in the Transvaal show a similar pattern. In the Lydenberg District magnesite crops out discontinuously in a belt more than 50 miles in length, stretching from the farm Welgevonden, about 30 miles N.N.W. of Lydenburg, past Burgersfort as far as Malips Drift on the Olifants river in the north. The occurrences closely follow the base of the B.I.C. and are derived from the surface or near-surface alteration of the ultrabasic rocks. Drainage exerts a strong influence on this process and thus the best deposits lie where the perennial Spekboom and Steelpoort rivers cross the basic periphery of the B.I.C., on the farms Aapiesdoorndraai, Aapiesboomen and Mooifontein. The ore generally occurs as large irregular bodies in peridotite and pyroxenite. The average composition of cobbed ore from

........../Burgersfort .....

Burgersfort is shown in Table II.

1.4.1.3. Sutherland Range

The Sutherland range is situated approximately 50 miles north of the Murchison range. The host rocks to the magnesite appear to be equivalent to those in which the Kaapmuiden-Malelane deposits are found. The average composition of the magnesite is also shown in Table II.

1.4.1.4. Marico District

In the Marico District a poor quality magnesite deposit is situated on the farm Rooikoppiesfontein, 40 miles to the north-east of Zeerust, where it occurs in pyroxenites of the Bushveld Complex.

1.4.1.5. Other South African Deposits

A number of deposits occur in the Zoutpansberg District. In the vicinity of Mopane and Messina veins of magnesite occur as a weathering product of pyroxenites. In the area extending eastwards from Tshipise larger bodies are encountered in limburgite of the Drakensberg Stage and in a sheet of olivine dolerite intrusive into the basal portion of the Karroo System. The magnesite is

........../present .....

present as veins and irregular masses and according to WILKE (op.cit.), was derived by the chemical weathering of the olivine-rich igneous rocks. Analyses of one sample from the Nyala Mine and two from the workings at Adieu are shown in Table II.

1.4.1.6. Newfoundland

In Central Newfoundland, 12 miles south of Gandar Bay, magnesite occurs in schistose and brecciated zones in peridotites, grading into serpentinites at the margins. The magnesite contains numerous quartz veins. (COOPER, 1957).

1.4.1.7. Greece

At Euboea in Greece magnesite occurs irregularly along shear and fracture zones in a serpentinite massif (BOYDELL, 1921). The mineralized zone forms a belt some 18 km long stretching across the island in an east-west direction and in some places the ore persists to a depth of at least 225 feet. Field and petrographic evidence indicates that magnesite and silica were formed by the alteration of serpentine through the activity of percolating meteoric waters rich in CO_2. A little chalcedony occurs on the surface but most of the silica must have been removed. The magnesite and partially replaced serpentine are both dense and the ore often inherits the slickensided, grooved appearance of the joint

........../surfaces .....

surfaces characteristic of the serpentine. Two analyses of the magnesite are given in Table II.

1.4.1.8. Poland

In Poland magnesite-quartz deposits have been described at Sobòtka (OSIKA, 1949) and Zobten (SPANGENBERG, 1949) in Silesia and at Grochowa and Braszowice in Slask (KRAJEWSKI, 1949). The ore is of the cryptocrystalline variety and occurs as large masses or as vein-fillings in shear zones. The magnesite has been attributed to hydrothermal alteration of the serpentinite host rock. For the deposits at Zobten, SPANGENBERG (op.cit.) has suggested that the solutions were derived from neighbouring granitic intrusions.

1.4.1.9. Yugoslavia

ILIC (1966a, 1966b, 1966c) on the other hand has postulated that the magnesite in the Kopoanik Region, Serbia, was formed by the alteration of serpentine by solutions emanating from propylitised dacite-andesite dykes. These deposits are associated with asbestos in serpentinized peridotites.

After a chemical study of the magnesite in the Maljensko-Suvolborsk serpentinite massif at Brezak in Yugoslavia, CMILJANIC (1970) concluded that the ore was formed by the action of ascending

........../hydrothermal .....

solutions.

1.4.1.10. Russia

The formation of magnesite by supergene alteration of ultrabasic rocks in Russia has been described in Armenia (ABOVYAN, 1957) and in Central Cisbaikalia (DOMBROVSKAYA, 1971).

1.4.1.11. Italy

In Italy the occurrence of compact, cryptocrystalline magnesite in serpentinized lherzolite has been noted near Ivrea and Torino (FENOGLIO and SANERO, 1941). Associated with the magnesite are veinlets and stringers of opal.

1.4.1.12. Tanzania

SAMPSON (1954) found magnesite veins of three different ages cutting a serpentinite body at Mwembe, near Same, Tanganyika (now Tanzania). The first two sets are evenly distributed throughout, while the third, which is the youngest and least pure, is concentrated around pegmatite bodies. Secondary silica, mostly chalcedony with minor quartz, occurs in the serpentinite and magnesite. Actinolite, chlorite and vermiculite are found in the youngest set of magnesite veins.

1.4.1.13. Japan

The Magnesite at the Mikawa Mine,

Yamaguchi Prefecture, Japan is an extensively deformed crystalline mass; it is considered to have been formed by the hydrothermal replacement of serpentinite. (KINOSAKI, 1961).

1.4.1.14. Philippines

SANTOS-YNIGO et al. (1961) have described magnesite concentrated at the extremities of seaward-jutting spears of an elliptical mass of peridotite at Piso Point in Pavao Province in the Philippines. The magnesite occurs as concretions or irregular, brain-shaped masses along open fractures in the host rock. Opalite is a common impurity in both types, and the latter also contains a high magnesium clay, possibly saponite. The authors consider the ore to have been formed by surface weathering processes. It appears that the magnesite was first deposited as sheets of hydrated colloidal $MgCO_3$ along with other colloids like Mg-rich clays and opaline silica, and that the complex wrinkles were later produced by shrinkage resulting from dehydration.

1.4.1.15. India

In India deposits of cryptocrystalline magnesite occur in ultrabasic rocks at Salem and Mysore (CROOKSHANK, 1941) and in the Quetta-Kalat and Peshawar Regions (VAN VLOTEN, 1962).

........../1.4.1.16 .....

1.4.1.16. Nevada

A rather unusual occurrence of magnesite occurs at Currant Creek, Nevada, where nodules and veins of magnesite are associated with dolomite, deweylite, calcite and quartz in vitreous volcanic tuffs. FAUST and CALLAGHAN (1948) consider the minerals to have been precipitated from a gel formed by the action on the host rocks of hydrothermal solutions rich in magnesium and bicarbonate ions.

1.4.1.17. California

HESS (1908) has described the occurrence of magnesite in serpentinites at numerous localities in California. The most important deposits occur in Mendocino, Sonoma, Napa, Alameda, Slanislaus and Santa Clara Counties in the Coast Range, along the west side of the Sierra Nevada Range in Placer, Fresno,Tulware and Kern Counties, and in southern California in Riverside County. He considered the magnesite to have been formed, together with limonite and quartz, directly from olivine, or via the intermediate formation of serpentine. In either case the alteration proceeds under the influence of surface or near-surface weathering, the magnesite being precipitated from solution due to the loss of CO_2 and the quartz being carried away in solution or deposited together with or close to the

........../magnesite .....

Two analyses of Californian magnesites are shown in Table II.

BAILEY and EVERHART (1964) have described in detail the alteration of serpentinite to a silica-carbonate rock. The serpentinites act as the host rock to the quicksilver deposits of the New Almaden District in California. Some of the small sheared serpentinite bodies have been completely replaced by the silica-carbonate rock, but the larger, more massive ones are altered only along their sheared margins. The alteration has been found to persist down to at least 1750 feet below the surface.

The silica-carbonate rock generally retains the sheared structure of the original serpentinite and also contains tiny residual grains of unaltered chromite and picotite. Quartz is by far the most abundant silica mineral, with very minor opal and chalcedony. The carbonate is mostly ferroan magnesite with a little dolomite occurring in veinlets. The overall colour of the rock is green or greenish-grey.

Most of the serpentinite host rock was derived from a harzbergite containing olivine and orthopyroxene; the alteration of lherzolite, which contains clinopyroxene in addition, was responsible for the remainder. The serpentinite consists essentially of a mesh of chrysotile and antigorite after olivine, bastite pseudomorphs after pyroxene,

........../and .....

accessory Chromite, magnetite and picotite. The authors suggest that the serpentine may have been formed in depth from a solid peridotite by a process of replacement accompanied by the escape of Mg and Si. Subsequently it has broken up and been squeezed plastically into its present position.

Microscopic study of the fresh and altered serpentinite reveals the general sequence of alteration to be the early replacement of the serpentine mesh by magnesite, followed by the replacement of the bastitic pseudomorphs. With continued alteration, the remaining serpentine is replaced by quartz, which may even replace some of the carbonate in cases of intense alteration. Late quartz and dolomite fill small fractures. The magnetite of the serpentine disappears at an early stage, the iron probably being incorporated into the magnesite. Textural features indicate that this process occurred under constant volume conditions. Chemical analyses, together with the specific gravities of the rocks, show that the alteration process involved the addition of CO_2 and the removal of water and a little magnesium. A small amount of calcium was introduced at a late stage during the formation of the dolomite.

The general equation for the conversion of serpentinite to silica-carbonate rock is :

$H_4Mg_3Si_2O_9$ + $3CO_2$ = $3MgCO_3$ +

(276g; 110c.c.) (252g; 84c.c.)

$2SiO_2$ + $2H_2O$

(120g; 44.5c.c.)

This would, however, involve an increase in volume and, since the chemical analyses show a loss of magnesium, the reaction can be rewritten as :

$H_4Mg_3Si_2O_9$ + $3CO_2$ = $2.34MgCO_3$ +

(276g; 110c.c.) (198.6g; 65.5c.c.)

$2SiO_2$ + $2H_2O$ + $0.66MgCO_3$

(120g; 44.5c.c.) (removed in solution).

The latter equation agrees very closely with the proportions of quartz and magnesite in the silica-carbonate rock.

BAILEY and EVERHART (op.cit.) conclude that the alteration was caused by hydrothermal solutions, which are unrelated to the origin of the serpentine.

BARNES et al. (1973) have noted numerous similar occurrences of silica-carbonate rock derived from serpentinite in the California Coast Ranges. CO_2-rich fluids are invariably associated with such deposits and, in an attempt to determine the origin of the fluids and whether or not they are responsible for the alteration, these authors have analysed chemically and isotopically the gases and waters from springs in the vicinity of the silica-carbonate rocks.

Two types of CO_2-rich waters were found, both of which are distinguishable from ground waters resulting from atmospheric precipitation and from the waters resulting from the weathering of serpentinite. The high-CO_2 waters generally have high HCO_3^- contents (between 1000 and 13000 mg/l), pH values below 7 and an average pCO_2 of approximately 1 atm. Because of the presence of free CO_2 the waters would remain acidic at higher temperatures. In addition, they show enrichment of δO^{18}, δD, Cl^-, CO_2 and HCO_3^- relative to the associated meteoric waters; δD values relative to the SMOW standard are negative, while the δO^{18} values of some are negative and others positive. With one exception, CO_2 is the dominant component of the gases bubbling up through the spring orifices.

A comparison of the analyses with thermodynamic data shows that 6 of the 9 samples of CO_2-rich waters are supersaturated with magnesite, 5 with dolomite, 4 with siderite and all with quartz, chalcedony and cristobalite; all are close to saturation with amorphous silica. The waters are unsaturated with respect to serpentine, diopside, forsterite, fayalite, clinoenstatite, talc and

........../tremolite .....

tremolite.

BARNES et al. (op.cit.) conclude that the silica-carbonate rocks are formed by the action of acidic CO_2-rich waters on serpentinite, the CO_2 having been derived from metamorphic reactions in depth. Isotopic data indicate that the waters are mixtures of meteoric and metamorphic waters and that reaction did not occur above 100°C; the upper limit of the reaction temperature is based on estimated values of δO^{18} for magnesite from the Red Mountain deposit. The dominance of quartz and chalcedony indicates that the temperature of formation was in excess of 55°C.

1.4.2. Magnesite-talc Deposits

The intimate association of talc and magnesite in a fine-grained assemblage known as talc-carbonate rock is widely accepted as being of low-grade metamorphic origin. The host rock is invariably serpentinite, although talc-carbonate rocks are less commonly found in association with the magnesite-quartz paragenesis.

1.4.2.1. South Africa

In South Africa talc is found associated with magnesite in a few localities in the Barberton area. HALL (op.cit.) attributed the origin of the assemblage to the following reactions occurring under the influence of carbonated ground waters :

......./ 4 .....

$4MgSiO_3 + H_2O + CO_2 = H_2Mg_3Si_4O_{12} + MgCO_3$

enstatite talc magnesite

$2Mg_2SiO_4 + 2SiO_2 + CO_2 + H_2O = H_2Mg_3Si_4O_{12} + MgCO_3$

olivine talc magnesite

Neither Hall nor VAN ZYL et al. (op. cit.) noticed any striking differences between the talc-magnesite and quartz-magnesite deposits, although in one locality, at Rockvale Siding, Van Zyl et al. (1942) describe a talc schist bordering a shear zone in the serpentinite.

1.4.2.2. Serbia

At Skoplie in Serbia cryptocrystalline magnesite is distributed in lens-shaped veins or pockets varying from small nodules to irregular masses of 50 to 100 tons in serpentinized peridotite. (IGNATIEFF, 1930). The mineralization is situated within well defined zones and does not persist in depth. Small amounts of talc occur in the host rock and ocassional small nodules of quartz. IGNATIEFF (op.cit.) suggests that the magnesite was formed principally by the action of carbonated hydrothermal solutions on the peridotite according to the following reactions :

$2M_2SiO_4 + 2H_2O + CO_2 = 2H_2O.3MgO.2SiO_2 + MgCO_3$

forsterite serpentine magnesite

........./4 .....

$4MgSiO_3 + H_2O + CO_2 = H_2O.3MgO.4SiO_2 + MgCO_3$

enstatite talc magnesite

$Mg_2SiO_4 + 2CO_2 = 2MgCO_3 + SiO_2$

forsterite magnesite quartz

The mineralizing solutions were regarded as late differentiates of the peridotite magma.

1.4.2.3. Sweden

Magnesite-talc deposits occur at a number of localities in the ultrabasic rocks of northern Sweden. On the basis of a thin-section study, DU RIETZ (1937) inferred the following sequence of alteration :

olivine → chrysotile → tremolite → chlorite → antigorite → talc → carbonates (chiefly breunneritic magnesite).

He attributed the alteration to the action of hydrothermal solutions emanating from acid intrusions. Two analyses of the magnesite are shown in Table II.

1.4.2.4. New Zealand

WELLMAN (1942) has described talc-magnesite and quartz-magnesite rocks in serpentinite in the Cobb-Takaka District, South Island, New Zealand. The field, mineralogical and chemical evidence that the rocks were formed by a progressive alteration of serpentinite, through talc-carbonate schist, to compact, coarsely crystalline magnesite containing much quartz. Such a process would involve continuous carbonation and dehydration. WELLMAN has calculated that if serpentine is completely altered to talc and magnesite the product would contain 39% $MgCO_3$ and 61% talc; if the process was continued the resultant assemblage would consist of 67,3% $MgCO_3$ and 32,7% quartz. These theoretical results accord well with the observed changes.

1.4.2.5. Scotland

AMIN (1952) has noted the occurrence of talc-magnesite-chlorite rocks along thrust zones in serpentinites in the Shetlands. He considered the tectonic deformation to have been accompanied by the passage of hydrothermal fluids along the movement planes and the transformation of the serpentine to chlorite, talc and magnesite.

1.4.2.6. Australia

Near Kunwarara, Queensland, veins, lenses and irregular masses of magnesite occur in an altered chlorite-mica schist near the contact with a dioritic intrusion (CUTTLER, 1958).

............/1.4.2.7. .....

1.4.2.7. The Sudan

Magnesite is found associated with talc in altered serpentinites in the Ingessana Hills in the Republic of the Sudan. KABESH (1961), on the basis of a chemical study, attributes the assemblage to alteration of serpentine by CO_2 metasomatism.

1.4.2.8. Egypt

The Egyptian talc-carbonate deposits and associated serpentinites have been described by BASTA (1969). The talc-carbonate rocks consist mainly of talc and magnesite or magnesite, dolomite and talc, together with minor amounts of antigorite, magnetite, goethite and, occasionally, chlorite or calcite.

1.4.2.9. Vermont

A detailed description of the talc-magnesite assemblages at Barnes Hill, Waterbury Mine and Mad River in north-central Vermont has been given by CHIDESTER (1962). At all three localities the talc-carbonate rock surrounds a central core of serpentinite and is itself surrounded by a zone of steatite. The carbonate consists mostly of ferroan magnesite with minor dolomite, and comprises approximately half of the talc-carbonate rock. All the minerals are of low-grade metamorphic origin (upper greenschist facies). The geologic

........../evidence .....

evidence indicates that serpentinization was earlier than and unrelated to the steatization, and that the talc-carbonate rock and steatite are of the same age, although formed by distinctly different reactions. The alteration of serpentine to talc and magnesite was accomplished very nearly on a volume for volume basis. Comparison of equal volumes of the various alteration products by means of a modified standard cell (devised to contain approximately 100 cations) discloses that the only chemical changes involved are the addition of CO_2 and loss of H_2O. The general equation for the reaction can thus be written :

$$\underset{\text{serpentine}}{2(Mg,Fe)_3Si_2O_5(OH)_4} + \underset{\text{magnetite}}{x(Fe^{2+},Mg)Fe^{3+}_2O_4} + 3CO_2 =$$

$$\underset{\text{talc}}{(MgFe)_3Si_4O_{10}(OH)_2} + \underset{\text{magnesite}}{3(MgFe)CO_3} + \underset{\text{magnetite}}{y(Fe^{2+},Mg)Fe^{3+}_2O_4} + H_2O$$

NALDRETT (1966) reached the same conclusions regarding the formation of the talc-carbonate rocks south of Timmins, Ontario.

1.4.2.10. Ontario

The most recent description of talc-magnesite occurrence has been given by GRIFFIS (1972), who studied the Deloro deposit near Timmins. He recognized four distinct mineral assemblages :

(a) serpentine country rock with minor magnesite

(b) fine-grained magnesite, talc, serpentine and

........../accessory .....

accessory iron oxides (c) fine-grained magnesite and quartz with minor talc and hematite and (d) medium-grained magnesite, talc, quartz and accessory iron oxide minerals. Petrographic evidence suggests that these assemblages represent respectively various stages in the progressive alteration of serpentinite. Chemical data indicates that negligible amounts of magnesia were added to or removed from the system during alteration and that a little silica may have been removed during the early stages of carbonatization. GRIFFIS (op.cit.) suggests that during the early stages of alteration temperatures were between 150° and 300°C, and that the medium-grained magnesite-talc-quartz assemblage may have been formed by decarbonatization and the crystallization of a second generation of talc under the influence of a rise in temperature and/or a decrease in the mole fraction of CO_2 in the hydrothermal fluids.

1.4.3. Magnesite associated with Sediments

Magnesite has been identified in Modern and Recent lacustrine, evaporite and speleothem deposits. In such environments the magnesite is almost invariably associated with one or more of the following : dolomite, brucite ($Mg(OH)_2$), nesquehonite ($MgCO_3.3H_2O$) hydromagnesite ($3MgCO_3.Mg(OH)_2.3H_2O$), or huntite ($CaMg_3(CO_3)_4$). Although the details are not yet clear, it appears that in these environments the mineral is either precipitated directly from solution or results from the early diagenetic alteration

........./of .....

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some precursor. The origin of large bodies of crystalline magnesite associated with older sediments - which represent the most valuable economic deposits - is more problematical. They have been interpreted as primary sediments and as the products of the metasomatic replacement of limestones and dolomites; in many cases these two contradictory views have been proposed for the formation of the same deposit by different workers.

1.4.3.1. British Columbia and California

BAIN (1924) has described two Recent sedimentary deposits of magnesite : one at Atlin, British Columbia and the other in the Mohave desert, Kern County, California. The former consists largely of hydromagnesite and occurs in a bed 6 to 8 feet thick over an area of 18 acres. The chemistry of the Kern County deposit indicates that it also contains some hydro-magnesite. The body displays a distinct bedded structure and is interstratified with clays and clay shales. The magnesite is fine-grained, breaking with a conchoidal fracture. Analyses of samples from these deposits are shown in Table II.

1.4.3.2. Salt Lake Desert

GRAF et al. (1961) have found a magnesite-like material in the sediments of the Great Salt Lake Desert, which forms part of the former glacial Lake Bonneville. A series of samples were collected from below the surface in a traverse from the former shore to the deepest parts of the lake. Sediments consisting for the most part of very fine grained mixtures of calcite, aragonite, dolomite and quartz

........../ were .....

were found in the deeper parts of the basin. A thin layer composed largely of micron-size dolomite particles occurs about one foot below the surface; closer to the shore and at the same depth the dolomite is replaced by 'magnesite' and aragonite. It appears that magnesium-containing carbonates are either chemical precipitates or diagenetic alteration products and that they were formed at a time of reduced water level when the lake was drying up. The 'magnesite' has a markedly enlarged unit cell, which GRAF et al. (op.cit.) tentatively attributed to an intimate association of water with the carbonate.

1.4.3.3. Australia

A very similar occurrence is located in the present-day shallow lakes of South Australia, which, together with the Coorong Lagoon, are strung out in a half-moon shape parallel to the south-east coast (ALDERMAN and VON DER BORCH, 1960, 1961 and VAN DER BORCH, 1965). The lakes occupy low-lying interdunal areas and are separated from the Southern Ocean by a sand dune barrier; they are ephemeral, filling annually with saline run-off and ground water during the winter months and evaporating to dryness during the summer.

VAN DER BORCH (op.cit.) has recognised six distinct carbonate assemblages occurring in the lakes : magnesian calcite-disordered dolomite,

........../magnesian .....

magnesian calcite-aragonite, magnesian calcite, well-crystallised dolomite, hydromagnesite-aragonite, and magnesite-dolomite. Each of these assemblages is found in a characteristic environment. The magnesite has an expanded unit cell and has been compared with the material found in the Great Salt Lake Desert.

Hydromagnesite is associated with aragonite in the surface deposits of at least two of the lakes. The waters of these lakes are milky and free from aquatic flora, and show a very low Ca content and high bicarbonate content compared with other lakes. Laboratory experiments with normal sea water show that the addition of sodium bicarbonate causes aragonite formation until the Ca content reaches 0.1% of the total salt, whereupon the precipitation of aragonite ceases and that of hydromagnesite commences and the water pH reaches a value of about 9.

The magnesite dolomite assemblage has also been observed in two of the lakes, whose main characteristics are very similar to those of the aragonite-hydromagnesite lakes, except for a significantly higher pH due to the presence of aquatic plant life. This assemblage may have been formed either by direct precipitation from saline waters or as a result of post-depositional alteration of an aragonite-hydromagnesite pair.

........../1.4.3.4. .....

1.4.3.4. Tunisia

PERTHUISOT (1971) has reported the occurrence of magnesite and huntite at the contact of a gypseous bed with carbonate muds in the Melah de Zarzis depression, Tunisia. The two minerals occur as crystals 1 to 2 microns in diameter in a bed of white, sticky mud which rarely exceeds 1m in thickness. Some calcite is also present, but no dolomite.

1.4.3.5. Central and eastern Europe and Central Africa

MUELLER et al. (1972) have recognised two types of Ca-Mg carbonates occurring in the lacustrine environment : primary precipitates (calcite, high-Mg calcite, aragonite and hydrous Mg-carbonates) and secondary minerals (dolomite, huntite and magnesite), which are derived from the former. In both cases the species formed is dependent on the Mg/Ca ratio of the lake or pore water. Thus, at Mg/Ca ratios of less than 2 low-Mg calcite is precipitated, at ratios between 2 and 12 high-Mg calcite and a little aragonite is formed, and at values in excess of 12 aragonite is the only carbonate precipitate; the hydrous Mg-carbonates are produced at very high Mg/Ca ratios.

The secondary minerals are formed by diagenesis only in lakes in which both the Mg/Ca ratio is high and high-Mg calcite is found. Dolomite appears to form at ratios of between 7 and 15 by the transformation of high-Mg calcite. The

........../available .....

available evidence concerning the formation of huntite and magnesite is rather scanty, but it seems likely that huntite is derived from dolomite and magnesite from huntite. In the lakes studied by these authors huntite and magnesite were found only in highly saline waters in which the pH varies from 7.0 to 8.5.

1.4.3.6. Yorkshire

The occurrence of magnesite in the evaporite environment has been recorded by STEWART (1949) near Aislaby, Eskdale, East Yorkshire. Magnesite occurs in two zones in the 460-foot thick Permain evaporite sequence : in the lower anhydrite zone, where it is associated with anhydrite, talc and halite and in the upper anhydrite layer together with dolomite. Textural characteristics indicate that the magnesite in the lower horizon was formed by the replacement of anhydrite when the rock was at least partially solid, and that the magnesite associated with dolomite was produced by the action of brines rich in $MgSO_4$ on dolomite, according to the equation :

$$\underset{}{MgSO_4} + \underset{\text{dolomite}}{CaMg(CO_3)_2} = \underset{\text{magnesite}}{2MgCO_3} \quad + \quad \underset{\text{anhydrite}}{CaSO_4}$$

1.4.3.7. Germany

In their description of the occurrence

........../ of ......

monohydrocalcite, hydromagnesite, nesquehonite, dolomite, aragonite and calcite in speleothems in Germany, FISHBECK and MüLLER (1971) have compared the deposits with those found in larger environments in which evaporation exceeds precipitation (for example, salt lakes and tropical lagoons). These authors conclude that the formation and diagenetic alteration of the minerals are governed mainly by the Mg/Ca ratio of the solutions from which precipitation or transformation takes place. It appears that calcite is the only phase precipitated when Mg/Ca is less than 1.45. Above this level some aragonite is formed together with the calcite until the ratio reaches 2.91, where aragonite is the dominant phase; at ratios greater than 4.36 aragonite only is precipitated. The hydrated magnesium carbonates form at ratios above 16, in which range conditions for the transformation of Ca-carbonates into dolomite are very favourable.

1.4.3.8. Texas

The formation of calcite, argonite domomite, hydromagnesite and huntite in nodular and flowstone speleothems in the Carlsbad Caverns has been described by THRAILKILL (1971). With two exceptions, all the samples containing hydromagnesite contain no other mineral, suggesting that hydromagnesite is being precipitated from solution and is not an

.........../ alteration .....

alteration product of some precursor. Analyses of the solutions, however, show that they are considerably undersaturated with respectto hydromagnesite and the precipitation of this mineral is difficult to explain.

The solutions are approximately saturated with respect to all the other minerals. Huntite was found in only two samples, where it is associated with hydromagnesite and it is assumed that one is formed from the other. Dolomite is assumed to form from aragonite in contact with Mg-rich waters, and there is also some evidence for the alteration of hydromagnesite to dolomite. Both calcite and aragonite are apparently being precipitated from solution : aragonite at low Ca/Mg ratios in the solution and calcite at high values.

BROUGHTON (1972) has briefly reviewed the literature concerning moonmilk, a soft, white, plastic substance frequently found coating the walls of certain caves. It is generally composed chiefly of calcite or hydromagnesite associated with organic filaments or bodies; dolomite, aragonite, huntite and nesquehonite are common accessory minerals. Numerous authors have pointed out the importance of microorganisms in the formation of these mineral species.

1.4.3.9. Australia

In Australia the occurrence of magnesite in the Pre-Cambrian sedimentary Adelaide System has been described by MAWSON (1947), SPRY (1952), SPRIGG (1952) and FORBES (1960, 1961). The Montacute Dolomite Formation serves as the host rock in which the magnesite occurs as a conglomerate bed varying in thickness up to 15 feet and often traceable for many miles. MAWSON (op.cit.) regarded the magnesite as having been deposited in shallow saline basins as thin beds which were later fragmented and redeposited as pellets. FORBES (op.cit.) noted the association of the magnesite with mud-cracked beds and considered it to have been deposited in the paralic zone, possibly by the precipitation of $MgCO_3$ as a result of the interaction of alkaline waters of continental origin with sea water.

1.4.3.10. Rhodesia

MAC GREGOR (1968) has described the magnesite at Gatooma, Rhodesia. The magnesite is dense, cryptocrystalline and massive and occurs in the form of a bed brecciated and veined by dolomite. Unequivocal evidence for either a sedimentary or replacement origin is insufficient, although MAC GREGOR (op.cit.) has noted numerous similarities with the magnesite in the Adelaide System of Australia.

1.4.3.11. India

In southern Pithoragarh in the Kumaun

of India, a chain of lens-shaped deposits of coarsely crystalline magnesite extends for at least 130 km north-west from the Kali Valley to the Alaknanda Valley (VALDIYA, 1968). The deposits are restricted to a narrow stratigraphic level in the upper part of the Gangolihat Dolomite formation and are almost invariably associated with biohermal stromatolitic dolomites. The rock is composed predominantly of magnesite with small quantities of dolomite, siderite, breunnerite, chert and talc distributed uniformly throughout. The chemical composition is also very uniform, the average composition being shown in Table II. The deposits are bedded and frequently intercalated with dolomite horizons, although no gradation between the dolomite and magnesite has been observed. Relict stromatolite structures are common. VALDIYA (op.cit.) notes that a metasomitic origin has been proposed by numerous authors, but points out that the evidence is more compatible with the formation of the magnesite by the replacement of dolomite algal bioherms by Mg-rich saline waters. He considers the process to have occurred in a series of barred basins formed by biohermal activity; subsequent recrystallization during regional metamorphism would account for the coarse granularity.

1.4.3.12. Manchuria

In the Tahsichiao-Haicheng area of Manchuria an extremely rich deposit of coarsely

........../crystalline .....

crystalline magnesite crops out over a total distance of 150 km. (NISHIHARA, 1956). The magnesite is bedded, containing dolomite intercalations and occasional thin lenses of talc; in places the sequence attains a thickness of 300 m. The deposit forms part of the regionally metamorphosed Lower Proterozoic or Upper Archean Wutai System.

A metasomatic origin for the deposit has been proposed by NüMONY (1925) and by KATO (1929). These authors postulate the formation of the magnesite by the replacement of original dolomite by magnseium-rich hydrothermal solutions emanating from intrusive biotite granite bodies. This view is opposed by NISHIHARA (op.cit.), who suggests that the magnesite was precipitated with dolomite in a saline lagoon or sea under the influence of an arid or semi-arid climate.

1.4.3.13. Austria

A sedimentary origin has also been proposed for the deposits at Entachen in Salzburg, Austria (SIEGL , 1969), in Norway (PETRASCHECK, 1971) and in the Larrau region of France (VINCIENNE, 1961). In the last occurrence the magnesium is considered to have been derived from neighbouring ophiolites by hydrothermal leaching and delivered to the basin of deposition by hot spring waters.

........../1.4.3.14. ....

1.4.3.14. Washington

In northern Okanogan County, Washington, magnesite-bearing rocks crop out as irregularly shaped lenses ranging in thickness from 5 to 50 feet and in outcrop length from 100 to 1100 feet (FOX and RINEHART, 1968). The horizon occurs at the base of a Triassic (?) eugeosynclinal sequence of greenstone and metachert. The magnesitic rock is typically a fine- to medium-grained granoblastic aggregate of magnesite, dolomite and quartz, with accessory calcite, chlorite, mica, magnetite and pyrite. The magnesite appears to be ferroan, and the grain size ranges from $\frac{1}{4}$ to 4 mm. FOX and RINEHART (op.cit.) suggest that the deposits are sedimentary, although the magnesite has recrystallized and probably undergone some local hydrothermal redistribution.

1.4.3.15. South Africa

In South Africa magnesite associated with sedimentary rocks has been recorded at only one locality. VAN ZYL et al. (1942) described a crystalline magnesitic dolomite on the farm Grasplaats, some six miles east of Lilliput Siding between Louis Trichardt and Messina. The deposit occurs as a vein which varies in width from 2 to 5 feet and is approximately 250 yards long. The walls of the vein are gneissic in character, and both the vein and the host rock appear to be the

........./remnant .....

remnants of primitive sedimentary rocks which have been invaded and altered by the surrounding Old Granite. It seems that the vein was originally a limestone which has suffered hydrothermal alteration.

1.4.3.16. Quebec

The Kilmar deposits of Argentuil County, Quebec are situated in metamorphosed sediments of the Precambrian Grenville Series (BAIN, 1924). The magnesite occurs as lenticular masses in a partially replaced limestone body which is sandwiched between garnet, biotite and feldspathic gneisses and serpentinite. All the rocks have been intruded by two sets of basic dykes and by a set of more acid batholithic intrusions, whose age lies somewhere between that of the two sets of basic dykes. The ore is intimately mixed with between 5% and 30% dolomite and minor amounts of serpentine and brucite. An analysis of the ore is given in Table II. BAIN op.cit.) has concluded that the magnesite is a product of the metasomatic replacement of limestone by hot, aqueous Mg-rich solutions.

1.4.3.17. Italy

Magnesite occurs with Triassic dolomite and subordinate limestones in the Orther mountains, Zumpanel District in Italy. ANDREATTA (1957) has suggested that the deposits were formed as a result of Mg-metasomatism by thermal solutions associated

........../ with .....

with pre- or syntectonic magmatic activity : the magnesium was leached during dedolomitization in depth and magnesite formed by the replacement of dolomites in tectonically dislocated zones at higher levels.

1.4.3.18. Washington

The magnesite of Stevens County, Washington, was discovered in 1916 and until very recently constituted the most important mineral resource of the area (CAMPBELL and LOOFBOUROW, 1962). The deposits occur in the Stensgar Dolomite member of the Deer Trail group, a series of closely folded metasediments. Prior to folding the sediments were intruded by basic rocks now represented by greenstones and later by a granitic batholith. The magnesite is crystalline and varies in colour from black, through grey to white and pink or red. It occurs in masses in the dolomite ranging from a few pounds to millions of tons in weight : transition between the dolomite and magnesite may be gradual or abrupt. In one locality a large body of brucite is associated with the magnesite. The authors postulate that the ore resulted from a volume-for-volume replacement of the dolomite by hydrothermal solutions related in origin to the granite batholith, the magnesium having been derived by dedolomitization in depth.

1.4.3.19 Nevada

Crystalline magnesite is associated with brucite at Gabbs, Nye County, Nevada (SCHILLING, 1968). The deposits are contained in a fine-grained, laminated dark dolomite belonging to the regionally metamorphosed Triassic Luning Formation. The magnesite is coarse- to fine-grained and occurs intergrown with marmorized dolomite. Accessory minerals include tremolite, chlorite, forsterite, antigorite and diopside; sulphides are rare. SCHILLING (op.cit.) favours a hydrothermal origin for the system, although it has also been interpreted as a sedimentary deposit.

1.4.3.20. Russia

The occurrence of magnesite formed by the alteration of carbonate rocks by Mg-rich solutions in Russia has been described by RAZVED (1967). The most important deposits occur near Satka in the western Ural Mountains, where they are interbedded with Upper Proterozoic dolomites.

1.4.3.21. France

The deposits near Mortner, south-east France, are considered by GUITARD (1967) to have been formed by the preferential replacement of Cambrian limestones by Mg-rich hydrothermal solutions.

1.4.4. Sagvandite

Sagvandite is an extremely rare rock type

........../consisting .....

consisting almost entirely of bronzite and magnesite. BARTH (1926) has described two dome-shaped occurrences 50 - 100m in diameter at Balsfjord, Troms county in northern Norway. The rocks appear to have been intruded into the surrounding chlorite and mica schists, exhibiting a distinct contact metamorphic aureole. In places the sagvandites show a gradational contact with the country rock. Bronzite and magnesite are the principal constituents, with picotite, pyrite and talc occurring in accessory amounts. The bronzite, which constitutes about 90% of the rock, generally occurs as idiomorphic rods arranged in radial aggregates. It is also found as irregularly shaped grains forming, together with magnesite, a finer grained matrix to the rods. The magnesite occurs almost entirely as anhedral grains in the matrix; it contains approximately 10% $FeCO_3$ and no CaO.

BARTH (1930) considered sagvandite to be a magmatic rock in which primary magnesite crystallized from a magma formed by the assimilation of dolomite by an ultrabasic melt.

In a brief review of the problem, JOHANNES (1969) described how more recent studies in Norway have revealed the presence of anthophyllite + magnesite and talc + magnesite + forsterite assemblages in association with the enstatite + magnesite. Experimental work (See Section 1.4.6, Figure 4) indicates that these rocks are formed by CO_2- metasomatism.

1.4.5. General Studies

1.4.5.1. The Work of G.W. Bain

BAIN (1924) was the first to correlate

........./ the .....

composition, occurrence and mode of origin of the different types of magnesite deposit. He recognised four main types :

(a) Magnesite as a sedimentary rock.

(b) Magnesite as an alteration of serpentine.

(c) Magnesite as a vein filling.

(d) Magnesite as a replacement of limestone and dolomite.

(a) Magnesite as a sedimentary rock

Examples of this type of deposit occur at Atlin, British Columbia and Kern County, California. Bain considered them to be chemical precipitates which formed in lakes filled with brines rich in sodium carbonate and other soluble salts. The introduction of spring waters rich in magnesium salts, possibly $MgSO_4$, would have caused reaction between the $MgSO_4$ of the springs and the Na_2CO_3 of the lakes to produce relatively insoluble $MgCO_3$ and soluble Na_2SO_4. The deposits are characterized by a high ferrous to ferric iron ratio, which indicates reducing conditions during precipitation and burial before complete evaporation and exposure to the atmosphere.

(b) Magnesite as an alteration of serpentine

Bain attributed the origin of these deposits to the decomposition of olivine in peridotites, first to serpentine and subsequently to magnesite,

........../ by ......

by carbonated waters. The nature of this alteration, notably the lack of oxidized products and the intense penetrating power of the solutions, favours a hydrothermal origin for the waters.

(c) Magnesite as a vein filling

Examples of magnesite veins occur near West Beach, New Brunswick, where the vein cuts a grey chlorite schist, and at Bolton township, Quebec, where the magnesite forms a deposit between steatite on the one side and serpentine on the other. The veins were thought to represent the concentration of magnesite in fissures by precipitation from rising juvenile waters.

(d) Magnesite as a replacement of limestone

Magnesite of this type is coarsely crystalline and usually associated with variable amounts of dolomite and pale yellow or green serpentine. Examples occur in Veitsch, Austria; Stevens County, California; and Argenteuil County, Quebec. According to Bain these deposits were formed by the replacement of limestone through the agency of Mg-rich solutions of magmatic origin, by the following process :

> "The solutions carrying talc, serpentine, diopside, forsterite and chondrodite either as dissolved mineral matter or as simple solutions reacted with the limestones to set free CO_2 which immediately attacked the unstable magnesian minerals and solutions in the same manner it would a crystallized peridotite, the only difference being that in this case reaction could take place so much more readily."

BAIN, op.cit., p.425

The overall reaction for this process was considered to be :

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{calcite}}{2CaCO_3} + SiO_2 = \underset{\text{magnesite}}{2MgCO_3} + \underset{\text{wollastonite}}{2CaSiO_3}$$

This reaction was envisaged as taking place via a number of intermediate steps involving first the replacement of limestone by dolomite and the subsequent alteration of the latter to magnesite. Talc and serpentine are intermediate by-products.

1.4.5.2. The Work of M. Ilić

After extensive work on magnesite deposits in the Balkans and a survey of all known deposits, ILIĆ (1968) formulated the following genetic classification :

I Endogenetic (hydrothermal) deposits.

  Metasomatic type.
  Vein type.

II Transitional hydrothermal - sedimentary deposits.

  Bela Stena type.

III Exogenetic deposits.

  A. Sedimentary deposits.
    Saliferous type.
    Detrital type.

............/B. .....

B. Deposits resulting from weathering.

Infiltration type.

(a) Metasomatic Type

The deposits are represented by extensive beds, lenses or stocks of crystalline magnesite lying in limestones or dolomites as, for example, in Manchuria (Tahsichiao-Haicheng area), Korea (Goyui, Tanzenguu), the Soviet Union (Satkinskne, Savinskoe), Austria (Radenthein, Veitsch and Trieben), Czechoslovakia (Dúlbrava, Kosice), Spain (on the west Pyrenees), the U.S.A. (Stevens County) and Canada (Grenville, Quebec).

Ilić favours the mesothermal metasomatic view concerning the origin of deposits of this type. Magnesium is considered to have been leached from deeper lying dolomites or ultrabasic rocks by hot solutions containing carbonic acid, and magnesite formed by the replacement of limestones and dolomites at shallower depths. Evidence in support of this hypothesis includes :

(i) The mineral paragenesis. Commonly associated with the magnesite are dolomite, calcite, aragonite, siderite, talc, chlorite, quartz, barite, pyrite, chalcopyrite, galena, sphalerite, goethite, tetrahedrite and carbonaceous matter, many of which are typical hydrothermal minerals.

........../ (ii) ......

(ii) Textural characteristics. The deposits frequently exhibit metasomatic textures such as banding and radially fibrous and stellar patterns.

(iii) The gradual increase in magnesium content from the surrounding carbonate rocks towards the ore bodies.

(iv) The close relationship in some localities between spathic magnesite and hydrothermal siderite deposits.

(v) Experimental studies supporting the chemical feasibility of the proposed process.

(b) Vein Type

This variety occurs as veins or stockworks of cryptocrystalline magnesite in ultrabasic rocks. Such deposits are abundantly represented in the Balkans and also at Euboea, Greece; the Soviet Union (on the Urals, southern Siberia), Austria (Kraubath), Poland (Lower Silesia), India (Madras), South Africa (Transvaal) and the U.S.A. (California).

Ilić points out that magnesite of this type was formerly taken to be the result of the weathering of ultrabasic rocks, but he considers the deposits to be of hydrothermal origin. This conclusion is based on the following :

(i) The considerable vertical extent and thickness of some of the magnesite veins. For example, in the Goles mine, Yugoslavia some

........./veins .....

veins have a length of 1200 m, a maximum thickness of 20 m and extend for over 300 m in depth.

(ii) Deposits of this nature are invariably closely associated with fault zones and volcanic activity (especially thermal springs).

(iii) The deposits are associated with definite tectono-magmatic cycles and accompanying mineralization epochs. The Balkan deposits, for example, were formed in the late stage of the Miocene Alpine volcanic cycle.

(iv) The microscopic, X-ray, d.t.a., spectrochemical and isotope examination of the Yugoslav deposits point to a hydrothermal origin.

(v) Evidence provided by the experimental study of carbonate systems.

As in the case of the metasomatic deposits the vein magnesites are considered to have been formed by the leaching of magnesium from underlying peridotites by hydrothermal solutions containing carbonic acid, and the subsequent deposition in the meso- to epithermal zone. The decomposition of the peridotites is thought to be accomplished by the following reactions :

$$2Mg_2SiO_4 + 2H_2CO_3 + H_2O = H_4Mg_3Si_2O_9 + Mg(HCO_3)_2$$

olivine serpentine

$$H_4Mg_3Si_2O_9 + 6H_2CO_3 = 3Mg(HCO_3)_2 + 2SiO_2 + 5H_2O$$

serpentine

........../ At ......

At shallower depths CO_2 is liberated from the bicarbonate either by release of pressure or by a change in the chemistry of the solution as a result of mixing with descending solutions, resulting in the precipitation of magnesium carbonate. The precipitation of the Yugoslav deposits is inferred to have occurred at $pH = 7.5$ to 9.5 and $Eh = -70$ to -120 mV.

(c) Bela Stena Type

Magnesite found in hydrothermal-sedimentary deposits is microcrystalline to cryptocrystalline, usually grey in colour due to the presence of organic matter and often intercalated with marls and shales. The results of microscopic, chemical and X-ray analyses of the ore show it to be very similar to vein magnesites, and it appears that these two types were formed during the same mineralizing epoch on the Balkan Peninsula. They are considered to have been produced by the leaching of Mg by ascending hydrothermal solutions and the subsequent escape of CO_2 and precipitation of $MgCO_3$ on the discharge of the solutions into lakes. Because of the unusual mode of formation of such deposits their occurrence is rare : they have only been recognized at Bela Stena, Beli Kamen, Silopaj, Lunjevica and Rvati in Yugoslavia, at Aiani in Greece, and at Bozkurt, Turkey.

(d) Saliferous Type

Saliferous magnesite deposits are

........../extremely .....

extremely rare owing to the special conditions necessary for their formation. Such deposits are found in the rock salt formations of Hall (Tyrol), Saint Pandelone (France) and Golf and Yorkshire in England. Experimental studies have shown that the precipitation of sedimentary magnesite is governed by :

(i) A relatively high concentrate of $Mg(HCO_3)_2$, known as the alkalinity or A. At 60°C the minimum concentration required is between 6 and 8 milliequalents per litre; this figure increasing with decreasing temperature.

(ii) A high concentration of CO_2 (>380 mg/l) and $CO_2/A \geqslant 2.2$.

(iii) Low calcium content of the water (<50mg/l).

(e) Detrital Type

Such deposits are formed by the mechanical disintegration of existing deposits and their redeposition in neraby basins. Deposits of detrital magnesite have been recognized only on the Balkan Peninsula at Janok and Badanj in Yugoslavia and at Euboea, Greece.

(f) Infiltration Type

Descending meteoric waters rich in carbonic acid leach Mg from the upper surfaces of ultrabasic

........../rocks, ...

rocks, transport it in the form of bicarbonate and deposit it in fissures and cavities at lower levels. A residual zone of ochers is thus formed at the surface, with a nontronite zone between the magnesite and the ochre zone. Deposits of this nature have a limited vertical extent and are of little economic significance. They have been observed at Halilovskoe in Russia, at Goles in Serbia and at Gro'ot near Titov Veles in Macedonia.

1.4.5.3. The Work of I. Lesko

In contrast to the emphasis placed on hydrothermal processes by Ilić, LESKO (1972) considers the features displayed by both microcrystalline and spar magnesites to be indicative of formation under low temperature earth-surface conditions.

(a) Microcrystalline Magnesite

Under favourable climatic conditions serpentine is decomposed by ground water containing dissolved CO_2, Cl^- and S^{2-}. Due to their solubility over a greater pH range (see Figure 1) the Mg^{2+}, Ca^{2+} and silicic acid ions remain in solution, while the oxides and hydroxides of iron are precipitated, together with Ni- and Cr- containing laterites. With increasing concentration of Mg^{2+} ions in solution the pH rises, resulting in the precipitation of $Mg(OH)_2$ and minor amounts of $Ca(OH)_2$ at pH values of about 11. The deposition of $Mg(OH)_2$ as a gel-like

........./mud .....

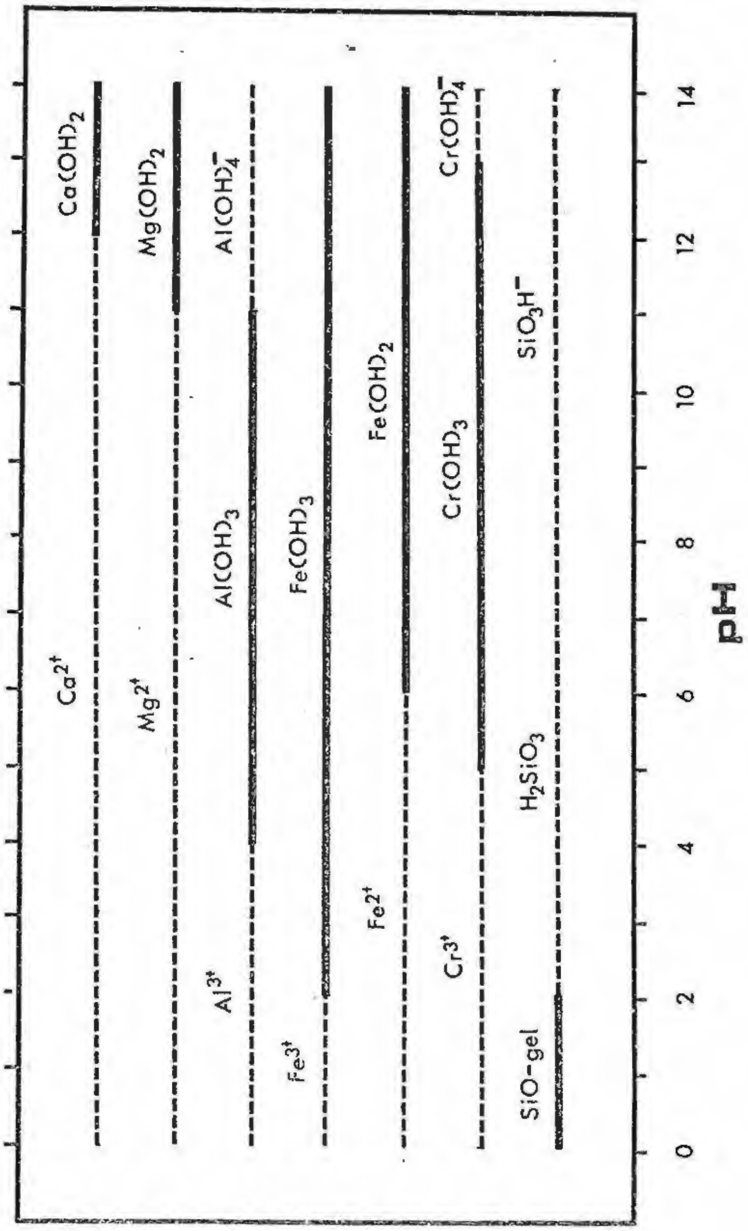

FIGURE 1 :

pH limits for the precipitation of selected species from aqueous solution at 25°C. (After LESKO, 1972.)

mud in cavities and fissures in the serpentinite results in the wellknown stockworks and kidney- and cauliflower-shaped masses. Under conditions of open drainage and a plentiful water supply most of the silica would be removed in solution; dehydration by evaporation, on the other hand, would cause the silica to be precipitated in close association with the Ca and Mg.

The subsequent formation of magnesite occurs through a stepwise recrystallization of the $Mg(OH)_2$ under the influence of dissolved CO_2, i.e. :-

$$Mg(OH)_2 \rightarrow MgCO_3.xH_2O \rightarrow MgCO_3$$

This process may occur at low CO_2 partial pressures and, since it involves dehydration and consequent volume decrease, results in the formation of highly porous magnesite.

Lesko cites the following as evidence in favour of the above process :

(i) The ease with which serpentine is decomposed by ground waters. Evaporation of water samples taken from the Kraubath serpentine area resulted in a residue of between 300 and 600 mg/l, with an average composition of :

MgO = 86%
CaO = 4%
SiO_2 = 5%
Al_2O_3 = 3%
SO_3 = 1%

........../Solid .....

Solid phases identified after evaporation at 70 - 100°C were hydromagnesite and aragonite; after drying at 20°C brucite, calcite, nesquehonite and an unidentified metastable carbonate were isolated. The pH of the water samples before evaporation varied from 8.4 to 9.0.

Solubility experiments with serpentinites and greenstones produced similar results after a few months.

(ii) The textures and structures in the magnesites indicate precipitation as a gel and subsequent dehydration.

(iii) The high porosity (5-25 vclume per cent) of the deposits.

(iv) The pseudomorphism of magnesite after metastable hydrated carbonates.

(v) The presence of hydrated carbonates in present-day deposits.

(vi) The small crystal size (4-10 mμ). At the high CO_2 partial pressures and high temperatures characteristic of hydrothermal conditions at least millimetre-size crystals would be formed.

(vii) The limited vertical persistence of the deposits.

............/ (b) .....

(b) Spar Magnesite

Lesko suggests that deposits of spar magnesite represent primary sediments deposited in an O_2- poor, H_2S-, CO_2-, NH_4- rich reducing environment, together with limestone, dolomite, pyritic and graphitic shales and occasionally salt deposits. The Mg may be derived from the weathering of Mg-rich minerals, either on the adjacent land mass or within the sedimentary basin itself. Precipitation of the Mg, mainly in the form of $Mg(OH)_2$ and $MgCO_3.xH_2O$, may occur under the influence of a high CO_2 content of the waters or the activity of microorganisms, or both. Subsequent burial resulting in increased temperatures and pressures would cause dehydration of the magnesite precursors and crystallization, giving rise to non-porous spar magnesite. The high Fe content of the magnesite is explicable in terms of the reducing milieu, which prevents the oxidation of Fe^{2+} to Fe^{3+}, thus enabling the ferrous ion to be incorporated into the carbonate structure.

Evidence favouring this hypothesis over the metasomatic replacement theory includes :

(i) The mineralogical and trace element content of spar magnesites. Quartz and small amounts of chlorite, carbonaceous matter and clay minerals are more abundant in the magnesite than in the surrounding limestones and dolomites,

.........../ indicating .....

indicating that the magnesite was not derived from the latter, but formed separately. In addition, the magnesites are generally found to contain larger quantities of certain trace elements, notably Mn, Sr, P and S, than the limestones and dolomites with which they are associated.

(ii) The presence of layered magnesite beds associated with other sedimentary rocks in tectonically undisturbed areas.

(iii) The occurrence of typical sedimentary structures such as ripple-marks and slump features in certain deposits.

(iv) The identification of magnesite in present-day sediments.

1.4.6. Laboratory Studies

Magnesite has proved to be extremely difficult to synthesize at low temperatures and pressures due to the preferential formation of the hydrated carbonates under these conditions (LANGMUIR, 1965). It can be produced by heating $CaCO_3$ with $MgCl_2$ solution (DEER et al. 1962) or by heating precipitated $MgCO_3$ with carbonated water in a sealed tube at 160° to 200°C (GOLDSMITH and GRAF, 1958).

Solubility and calorimetric determinations are also beset with difficulties and as a result divergent and conflicting solubility and thermochemical data have been quoted in the literature. LANGMUIR (op.cit.) has reviewed

........./ the .....

the situation and, using a value of $10^{-5.1}$ for the activity product constant, determined the probable stability relations of magnesite with respect to brucite, lansfordite, nesquehonite, artinite, hydromagnesite and periclase. These results are shown in Figure 2 (a), (b) and (c).

The diagrams indicate that the formation of magnesite rather than one or more of the hydrated phases is favoured by :

(i) High ionic strength in aqueous solution or low relative humidities of water vapour.

(ii) CO_2 pressures in excess of those normally existing in the atmosphere ($10^{-3.5}$ atm.). Most ground waters do, in fact contain more CO_2 than this.

(iii) Elevated temperatures (greater than 50° to 60° or less in dry environments).

LANGMUIR (op.cit.) notes that the occurrence of magnesite in evaporite deposits and as a product of the dessication of hydromagnesite in warm or dry climates is consistent with these conditions. In addition, magnesites of hydrothermal and metamorphic origin, as well as most sedimentary magnesites, have been subjected to sufficiently high temperatures and CO_2 pressures to stabilize the anhydrous carbonate.

More recent determinations of the activity product constant of magnesite, however, indicate that it is theoretically more stable than indicated by LANGMUIR. CHRIST and HOSTETLER (1970) obtained a value of $10^{-8.1}$ at 25°C, which compares very favourably with the values quoted

......../ by ......

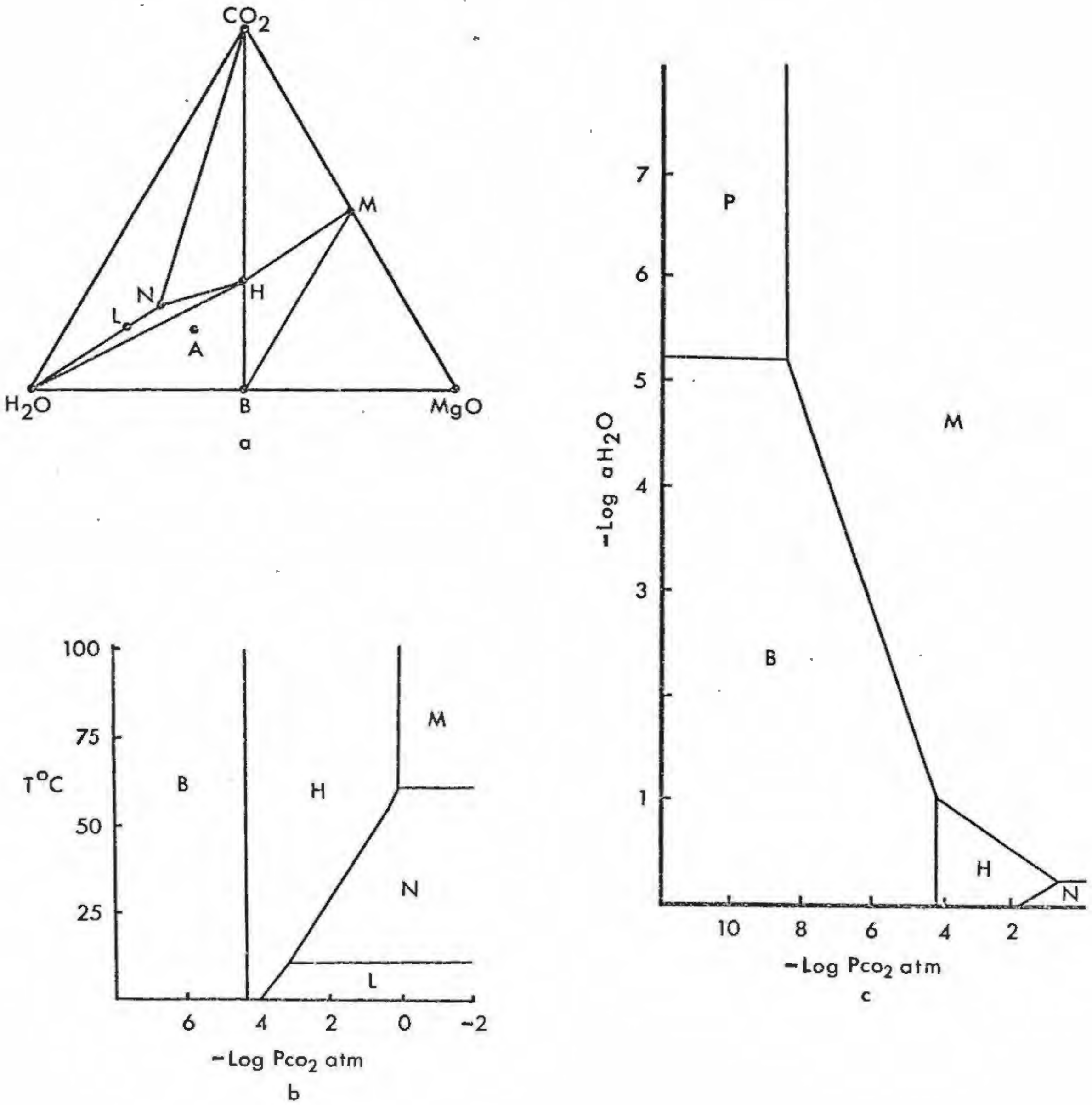

FIGURE 2 :

The system $MgO-CO_2-H_2O$. (a) Probable phase relations at 25°C and 1 atm total pressure. (b) Probable stability relations between 0° and 100°C as a function of $p(CO_2)$, assuming $aH_2O=1$. (c) Probable stability relations at 25°C and 1 atm total pressure as a function of $p(CO_2)$ and aH_2O. A, artinite; B, brucite; H, hydromagnesite; L, lansfordite; M, magnesite; N, nesquehonite; P, periclase. (After LANGMUIR, 1965).

by ROSSINI, et al.(1961) and ROBIE and WALDBAUM (1968). If this value is correct, then, contrary to the conclusions reached by Langmuir, magnesite rather than hydromagnesite or nesquehonite is the stable phase under earth surface conditions. This is in accordance with the fact that hydromagnesite and nesquehonite have never been recorded as an alteration product of magnesite.

The results of CHRIST and HOSTETLER (op.cit.) also indicate that the oceans and many natural terrestrial waters are supersaturated with respect to magnesite (and dolomite). The authors attribute the reluctance of magnesite to form from aqueous solution, both in the laboratory and in nature, to the strong hydration of the Mg^{2+} ion. This hypothesis is supported by the fact that most authigenic magnesite deposits seem to have been formed in very saline environments in which the activity of water would be markedly decreased.

SAYLES and FYFE (1973) investigated these ideas by studying the crystallization kinetics of magnesite using the reaction :

$$\text{hydromagnesite} + CO_2 \rightleftharpoons \text{Magnesite} + H_2O + \text{brucite.}$$

The experimental results support the proposals of CHRIST and HOSTETLER (op.cit.) and are also compatible with observations made by VON DER BORCH (1965,op.cit.) on the precipitation of magnesite in natural lakes.

CARPENTER (in Garrels and Christ, 1965) has constructed a diagram to show metastable and stable equilibria among the calcium and magnesium carbonates. These

........../ relations .....

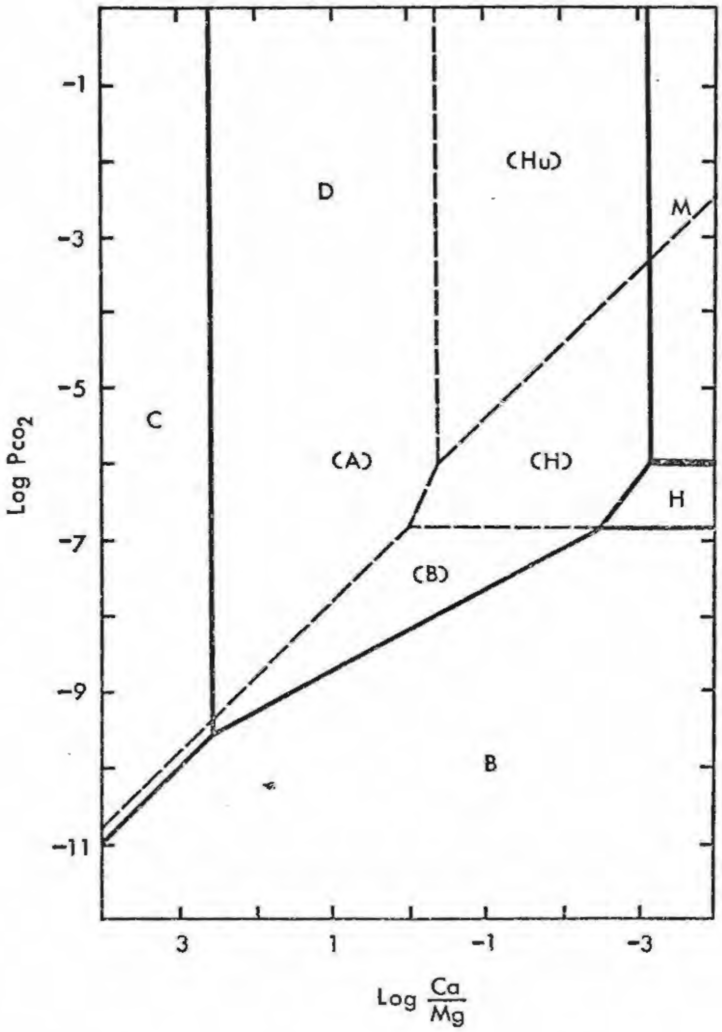

FIGURE 3 :

Relations among Ca and Mg carbonates at 25°C and 1 atm total pressure as a function of $P(CO_2)$ (in atm) and the relative concentrations of Ca and Mg. Solid lines show equilibrium relations between stable phases, dashed lines show metastable relations. A, aragonite; C, calcite; B, brucite; D, dolomite; H, hydromagnesite; Hu, huntite; M, magnesite. Metastable phases in parentheses. (After CARPENTER in GARRELS and CHRIST, 1965).

relations are shown in Figure 3, which indicates that for CO_2 pressures obtaining in the atmosphere brucite, aragonite, huntite and hydromagnesite are the first-formed minerals, which eventually equilibrate to give the phase relations shown by the solid lines.

Experimental work by ROY et al. (1953) shows that hydromagnesite becomes unstable relative to magnesite and brucite at some temperature between 185° and 240°C. IWAI et al. (1971) have achieved the transformation of nesquehonite to hydromagnesite and the latter to magnesite at 190°C and 35 kg/cm^2. It would appear, however, that these transformations take place at much lower temperatures and pressures in nature.

ROSENBERG, BURT and HOLLAND (1967) have determined the stability relations between calcite, dolomite and magnesite in aqueous $CaCl_2$- $MgCl_2$ solutions containing dissolved CO_2 between 275° and 420°C. They found magnesite to be stable at concentrations of the solution up to between 0.65 and 0.85 $mCa^{2+}/mCa^{2+}+mMg^{2+}$ at temperatures ranging from 300° and 420°C. At lower temperatures and greater concentrations of Ca^{2+} dolomite replaces magnesite as the stable solid phase.

On the basis of a study of mineral equilibria in the system $MgO-SiO_2-H_2O-CO_2$ GREENWOOD (1967) has concluded that the assemblage magnesite-quartz-talc is unstable, and that magnesite occurs either with quartz or talc, but never with both. Greenwood suggests that the chalcedonic or

....../ quartz- .....

quartz-bearing magnesite deposits form at low temperatures and probably in contact with water-rich CO_2-bearing solutions, whereas the talc-magnesite deposits form at temperatures that could be as high as 650°C (at 2 Kb) and in contact with solutions that may be either nearly pure CO_2 or nearly pure H_2O, or of any intermediate composition. The results also show that below 400°C and at 2 Kb serpentine is stable in contact with water only if the water is essentially pure; any addition of SiO_2 and/or CO_2 results in the formation of talc or magnesite.

In a study of the same system JOHANNES (1969) has established the equilibrium conditions for the following reactions :

1. 2 forsterite + $2H_2O$ + $CO_2 \rightleftharpoons$ serpentine + magnesite.
2. 4 forsterite + H_2O + $5CO_2 \rightleftharpoons$ talc + 5 magnesite.
3. 2 serpentine + $3CO_2 \rightleftharpoons$ talc + 3 magnesite + .$3H_2O$.
4. talc + $3CO_2 \rightleftharpoons$ 4 quartz + 3 magnesite + H_2O.
5. serpentine + $3CO_2 \rightleftharpoons$ 2 quartz + 3 magnesite + $2H_2O$.
6. 2 forsterite + $3H_2O \rightleftharpoons$ serpentine + brucite.
7. 2 forsterite + $2CO_2 \rightleftharpoons$ enstatite + 2 magnesite.

These relations are shown in Figure 4 : the conditions under which the reactions occur are shown by the respective numbers on the diagram. All reactions are discussed at a

.........../ fluid .....

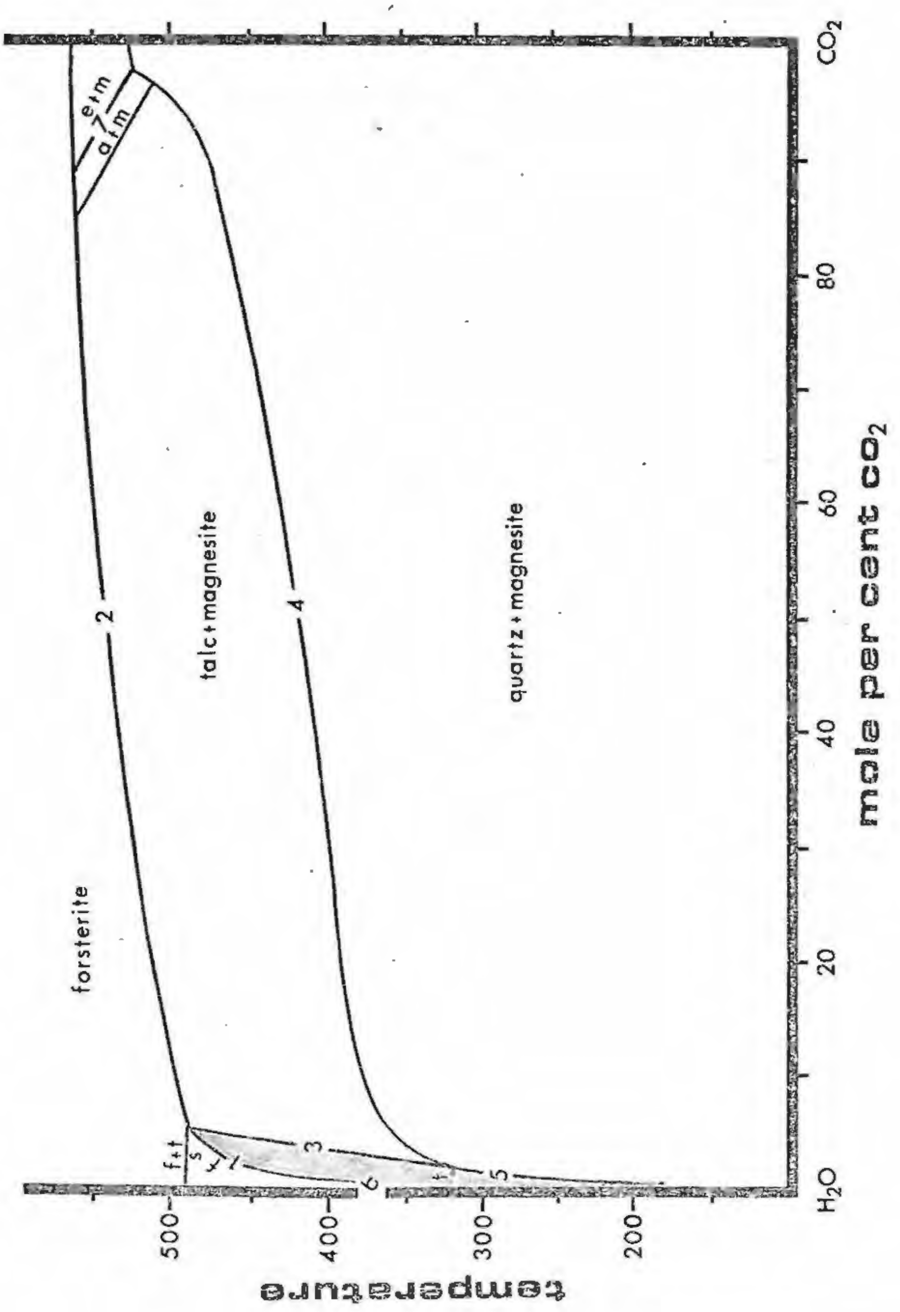

FIGURE 4 :

Stability relations in the system MgO-SiO_2-H_2O-CO_2 as a function of temperature and composition of the fluid phase. E, enstatite; M, magnesite; A, Mg-anthophyllite; T, talc; F, forsterite; S, serpentine; shaded area, serpentine + quartz. Numbers refer to reactions discussed in the text. (After JOHANNES, 1969.)

fluid pressure of 2 Kb. At higher pressures the equilibrium curves move to higher temperatures and at lower pressures they are displaced to lower temperatures.

Reactions 1 and 6 : The serpentinization of forsterite.

The equilibrium temperature for the formation of serpentine and magnesite by the action of H_2O and CO_2 on forsterite rises from 380° to 490° at 6%. This mode of formation of magnesite, however, is considered to be relatively unimportant, most magnesite deposits associated with ultrabasic rocks being produced by the alteration of serpentine according to reactions 3 and 5. Apparently the serpentinization of dunites and peridotites occurs mainly in a very CO_2-poor environment according to reaction 6. Brucite is only stable up to $X_{CO_2} = 0.5\%$ at 400°C; at higher values of X_{CO_2} reaction 6 is replaced by reaction 1.

Reaction 2 : The formation of talc and magnesite from forsterite, H_2O and CO_2.

This reaction occurs over a wide range of X_{cO_2}. JOHANNES (op.cit.) suggests that the talc-magnesite occurrences in ultrabasic rocks at Handöl, Sweden and at Aaheim, West Norway and in sagvandites in north Norway may have been formed by this reaction.

Reaction 3 : The formation of talc and magnesite from serpentine and CO_2.

Serpentine can exist only with a CO_2-poor fluid phase: as little as 1 to 3 mole per cent CO_2 is enough to cause reaction at 400° to 500°C.

........../Reaction ......

Reaction 4 : The formation of quartz and magnesite from talc and CO_2.

Like reaction 2, this reaction occurs over a wide range of X_{CO_2}, the equilibrium temperature increasing with increasing X_{CO_2}. The position of curve 4 indicates that in magnesite deposits containing quartz without any trace of talc temperatures did not exceed 300° or 400°C. In instances where the reaction of quartz and magnesite to form talc has been observed temperatures of at least 300°C have been reached. JOHANNES (op.cit.) quotes numerous instances where talc has been observed as a replacement of magnesite.

Reaction 5 : The formation of quartz and magnesite from serpentine and CO_2.

The position of reaction 5 shows that quartz and magnesite can be produced by the alteration of serpentine at low temperatures and very low CO_2 contents of the fluid phase.

Reaction 7 : The stability of the enstatite-magnesite assemblage.

Figure 4 shows that the paragenesis enstatite + magnesite is stable only below 560°C and at a very high CO_2 content of the fluid phase. This conflicts with Barth's suggestion (BARTH, 1930, op.cit.) that the magnesite in sagvandite crystallizes directly from a melt, since such a 'sagvandite magma' could exist only at temperatures in excess of 560°C. Johannes concludes that sagvandites are formed by CO_2-metasomatism according to reaction 7.

........../JOHANNES .....

JOHANNES (1966, 1967) has also investigated the transport of Mg in solution, both as a carbonate and as a chloride, in order to clarify the metasomatic formation of magnesite deposits. The results show that Mg-metasomatism can be much more easily accounted for if Mg is considered to be transported under the influence of chloride ions rather than in a CO_2-bearing fluid phase.

1.4.7. Conclusion

The experimental work of JOHANNES (1969, op.cit., See Section 1.4.6.) shows that the mineral assemblage quartz + magnesite is stable over a wide range of temperature - X_{CO_2} conditions. Although no information is available for this reaction below 200°C, extrapolation of line 5 in Figure 4 towards lower temperatures suggests that the alteration of serpentine to quartz and magnesite by carbonated waters may occur at Earth-surface temperatures and CO_2 concentrations commonly found in ground waters derived from the atmosphere. Such a conclusion is consistent with the field setting, texture and mineralogy of many quartz-magnesite deposits (See Section 1.4.1. and LESKO, 1972, op.cit. Section 1.4.5.) Figure 4 shows the upper stability limit of this reaction to be characterized by temperatures in the region of 400°C and composition of the fluid phase ranging from 5 to 95 mole per cent CO_2. The medium- to coarse-grained magnesite deposits described by WELLMAN (1942, op.cit.) and GRIFFIS (1972, op.cit.) appear to have been formed at or close to this limit by a process of CO_2-metasomatism (See Section 1.4.2.).

In the light of the preceding, it would seem

........../ rather .....

rather shortsighted to attempt to classify all quartz-magnesite occurrences as either the products of surface weathering or hydrothermal processes. BARNES and O'NEIL (1973), in fact, have shown that the silica-carbonate alteration of serpentine may be caused by various mixtures of hydrothermal and meteoric waters.

According to Figure 4 the talc-magnesite alteration of serpentine occurs at temperatures of around 400° to 500°C at low CO_2 concentrations in the fluid phase. These experimental observations agree with the conclusions reached by CHIDESTER (1962, op.cit.), NALDRETT (1966, op.cit.) and others regarding the formation of talc-magnesite aureoles around serpentinite (See Section 1.4.2.).

The position of curve 4 in Figure 4 shows that the quartz-magnesite assemblage is transformed to talc-magnesite with increasing temperature in the region of 350° to 450°C, and that the reverse reaction occurs within the same temperature range with increasing CO_2-content of the fluid phase. Again, the experimental results are in accordance with the interpretations of WELLMAN (1942, op.cit.) and GRIFFIS (1972, op.cit.) of naturally occurring quartz-magnesite, talc-magnesite and quartz-magnesite-talc assemblages. (See Section 1.4.2.).

Sedimentary magnesite has only been observed to form from saline solutions containing a high concentration of Mg/Ca. Such conditions are achieved by the evaporation of shallow lakes under the influence of arid or semi-arid climates or of ground waters in caves (See Section 1.4.3.). Whether these conditions could persist long enough to give rise to

......../ the .....

the large bodies of crystalline magnesite is open to doubt and some considerable controversy still surrounds the origin of these deposits (See Section 1.4.5.). Judging from some of the conflicting generalizations concerning the characteristics of the deposits made by proponants of the opposing theories, it is quite possible that some of the deposits have been formed by hydrothermal alteration and others by sedimentary processes.

Another problem that remains as yet unresolved concerns the mechanism of magnesite crystallization. It would appear that at high temperatures magnesite crystallizes directly from solution. Laboratory and field evidence suggests that at lower temperatures some factor, possibly the hydration of the Mg^{2+} ion, inhibits crystallization of the anhydrous carbonate (CHRIST and HOSTETLER, 1970, Section 1.4.6.). It seems that under such conditions magnesite is formed by the dehydration and/or recrystallization of an early-formed metastable phase (See Fig. 3). MÜLLER, et al. (1973, op.cit., Section 1.4.3.) attribute the formation of magnesite in saline lakes to the action of Mg-rich water on huntite. VON DER BORCH (1965, op.cit.), Section 1.4.3.) has postulated that the magnesite found in marginal marine lakes in S. Australia may either have been precipitated directly from solution or formed as the result of the alteration of an aragonite-hydromagnesite assemblage. LESKO (1972, op.cit., Section 1.4.5.) suggests that in Mg-rich waters derived from the supergene weathering of serpentine, brucite is the first Mg-rich phase to be formed; the action of CO_2-rich waters on brucite results in the formation of one or more hydrated phases, possibly hydromagnesite and/or

........./nesquehonite ......

nesquehonite, the dehydration of which result in magnesite.

It seems likely that sagvandites are formed by a process of CO_2-metasomatism during which the CO_2-content of the fluid phase is very high.

two

geology

2.1. Introduction

The farm Aapiesboomen is situated approximately 6 km west of Burgersfort on the main Lydenburg-Pietersburg road. It measures roughly 16 km^2 in area and is elongate in shape. The Hoosi river runs down the length of the farm in an easterly direction to join the Steelpoort river, which forms the eastern boundary.

Norites and pyroxenites of the Bushveld Igneous Complex give rise to a range of hills which covers the southern part of the farm, striking roughly parallel to the Hoosi river (See frontispiece).

............/Metamorphosed .....

Metamorphosed sediments of the Pretoria Series and concordant diabase sheets crop out in the Magaba hills immediately north of the Hoosi River. The magnesite deposits are situated on the flat plain between the river and the outcropping igneous rocks of the Bushveld Complex. These relationships are shown on the accompanying map.

With the exception of the south-eastern quadrant, the entire farm was mapped geologically to a scale of 1 : 25 000 by the late Professor Willemse (WILLEMSE 1950a, 1950b). During the present investigation this regional mapping was completed and the magnesite deposits mapped in detail and systematically sampled. The smaller occurrences were mapped rather roughly to a scale of 1 : 500 in order to obtain some idea of their size and to describe and analyse their characteristics. A baseline 1,3 km long was cut down the length of the main ore body (Locality XV) and perpendicular offsets cut through the bush at 50m intervals along this baseline; the body was then mapped to a scale of 1 : 2 000 and extensively sampled. Locality XIV was mapped to a scale of 1 : 2000 along a baseline cut during the drilling operations carried out by Goldfields of S.A. some three years ago. The mapping of Locality V to a scale of 1 : 1 000 was facilitated by extensive bush clearing performed during previous prospecting.

2.2. Regional Setting

Mention has already been made (See Section 1.4.1.) of the sporadic outcrops of magnesite which follow the base of the Bushveld Complex from approximately 3 km NNW of Lydenburg to the Oliphants river in the north. It has also been pointed out that the best deposits are situated where the perennial Spekboom and Steelpoort

............/ rivers ......

rivers cross the ultramafic margin of the Complex on Aapiesboomen, Aapiesdoorndraai and Mooifontein, near Burgersfort (VAN ZYL et al. 1942). To this should be added that the Burgersfort area is one of petrographic and structural irregularity when compared with the Bushveld Complex in adjoining areas, and has been subjected to strong faulting and fracturing. In a map illustrating the marginal features of the Complex in the Eastern Trasnvaal, WILLEMSE (1959) has shown that in the vicinity of Burgersfort the margin of the Complex forms a prominent loop extending outwards from the general strike and enclosing the so-called Hendriksplaas Norite and Aapiesdooring Peridotite. The map also indicates that the Steelpoort river may follow a prominent fault, from which numerous smaller faults branch out towards the north.

2.3. Previous Work

VAN ZYL et al. (1942) have described the magnesite on Aapiesboomen as a shallow blanket-like occurrence formed by the transpiration of magnesite-bearing ground waters through the soil. The presence of magnesite is generally indicated by the growth of a small, pale-green, berry-carrying bush and the absence of dense bush. The ore consists of cobbles of magnesite in the soil and subsoil ranging in size from less than an inch in diameter to over 8 inches. Silica occurs in a finely disseminated form invisible to the naked eye. The cobble ore is often overlain by so-called "blanket reef", a hard surface crustification containing considerable amounts of impure material.

WILLEMSE (1964) considered the deposit to have formed by the weathering of a layered peridotite body.

The deposit has been investigated on numerous occasions since the late 1930s

........../ but .....

but the ore has always been found to be uneconomic due to the high silica and lime content. In recent years interest was revived by the search for new magnesite reserves and the hope that some technique could be found for the beneficiation of the deposit. The present study was initiated as a result of this renewed interest.

2.4. Sediments

The Magaliesberg Group sediments of the Transvaal System underlie the Bushveld Complex in this area : these consist of alternating bands of shale, which contain numerous thin carbonate horizons, quartzite and concordant diabase sheets. All show strong thermal metamorphic effects.

2.5. Bushveld Complex

The map shows a slight discordance between the general strike of the Bushveld rocks and that of the underlying sediments, although the contact is very poorly exposed. A transgressive relationship is supported by observations made by WILLEMSE (1950b, 1964). Norites containing intercalated layers of pyroxenite and spotted norite and minor peridotite bodies are the only phases of the Complex occurring on Aapiesboomen. WILLEMSE (1950b) noted a very complex relationship between the floor of the Complex and the underlying rocks : in places the norites and peridotites appear to intrude the sediments.

2.5.1. Norite

The norites exhibit a chill phase at the contact : this is rather coarse-grained and characterised by the presence of biotite andusually quartz. Elsewhere the norites are feldspar-rich and usually hyperitic, containing dark green

............/ clinopyroxene .....

clinopyroxene in addition to the brown orthpyroxene. In general they weather far more easily than the pyroxenites and outcrop poorly. They contain numerous sedimentary xenoliths.

2.5.2. Pyroxenite

The pyroxenites are relatively resistant and are thus well exposed in the hills, where they form the dip slopes and stand out as prominent bands in the scarp slopes (See frontispiece). The lower horizons are generally feldspathic and richer in a green pyroxene.

2.5.3. Spotted norite

The spotted norite invariably occurs as a thin horizon at the contact between the pyroxenite bands and the norite. It would perhaps have been more aptly named a spotted pyroxenite in this area since it consists of a pyroxenitic groundmass containing noritic patches 1,5 to 2 cm in diameter. It exhibits a mottled weathering surface. WILLEMSE (1950b) considered this material to be a hybrid rock resulting from the intrusion of pyroxenite bands into the norite, which, on the field evidence, appears to be the first phase of the Complex to have been emplaced.

2.5.4. Peridotite

Small peridotite bodies are generally confined to the pyroxenite bands. Outcrops are extremely poor. The weathered surfaces are mottled and irregular and the rock has suffered moderate to intense serpentinization.

............/ 2.6. ....

2.6. Post Bushveld intrusives

2.6.1. Granite

This rock is represented by pod-shaped bodies and veins concentrated in fault zones. It is most commonly white in colour, displays a medium grain size and consists of quartz and potash feldspar in approximately equal amounts, and minor biotite. The granite intrudes both the Bushveld rocks and the underlying sediments : in the latter environment it often occurs as light pink coloured veins and a white pegmatitic phase containing large tourmaline crystals.

2.6.2. Dolerite

A swarm of narrow dolerite dykes cuts through the area in a general north-south direction. According to WILLEMSE (1950b) they are younger than the faults.

2.7. Structural geology

2.7.1. Faults

The Steelpoort river is thought to follow a major fault (WILLEMSE, 1950b, 1964) and the minor faults, which strike north-south, apparently branch out from the former.

2.7.2. Joints

A prominent set of near-vertical oblique joints strike parallel to the faults. Strike joints dipping at shallow angles (10° - 30°) are also well developed.

............/ 2. 8. ......

2.8. Magnesite deposits

The ore can be classified into five types : Skeletal ore, Zebra ore, Vein ore, Nodular ore, and Massive ore.

2.8.1. Skeletal ore

This type is characterised by a magnesite 'skeleton' occurring in the interstices between fragments of weathered host rock. The form of this skeleton depends upon the structural characteristics of the host rock : whether the latter is massive or jointed and, if jointed, on the number of joint directions, the width of the joints and the spacing between them. The host rock is most commonly pyroxenite and every gradation may be observed between thin films of magnesite surrounding individual pyroxene grains, to magnesite shells 2 to 5 cm thick enclosing boulders up to a foot in diameter. A typical example of skeletal ore is illustrated in Plate 1A.

2.8.2. Zebra ore

This consists of roughly parallel veins and stringers of magnesite, varying in width from less than 1 mm to 1 cm, separated by relicts of weathered host rock of the same thickness. The latter is generally more highly weathered than that associated with the skeletal ore and consequently more difficult to identify : in the trench illustrated by Plate 1B the host rock is serpentinized peridotite.

2.8.3. Vein ore

Vertical or steeply dipping veins of magnesite

........./ often .....

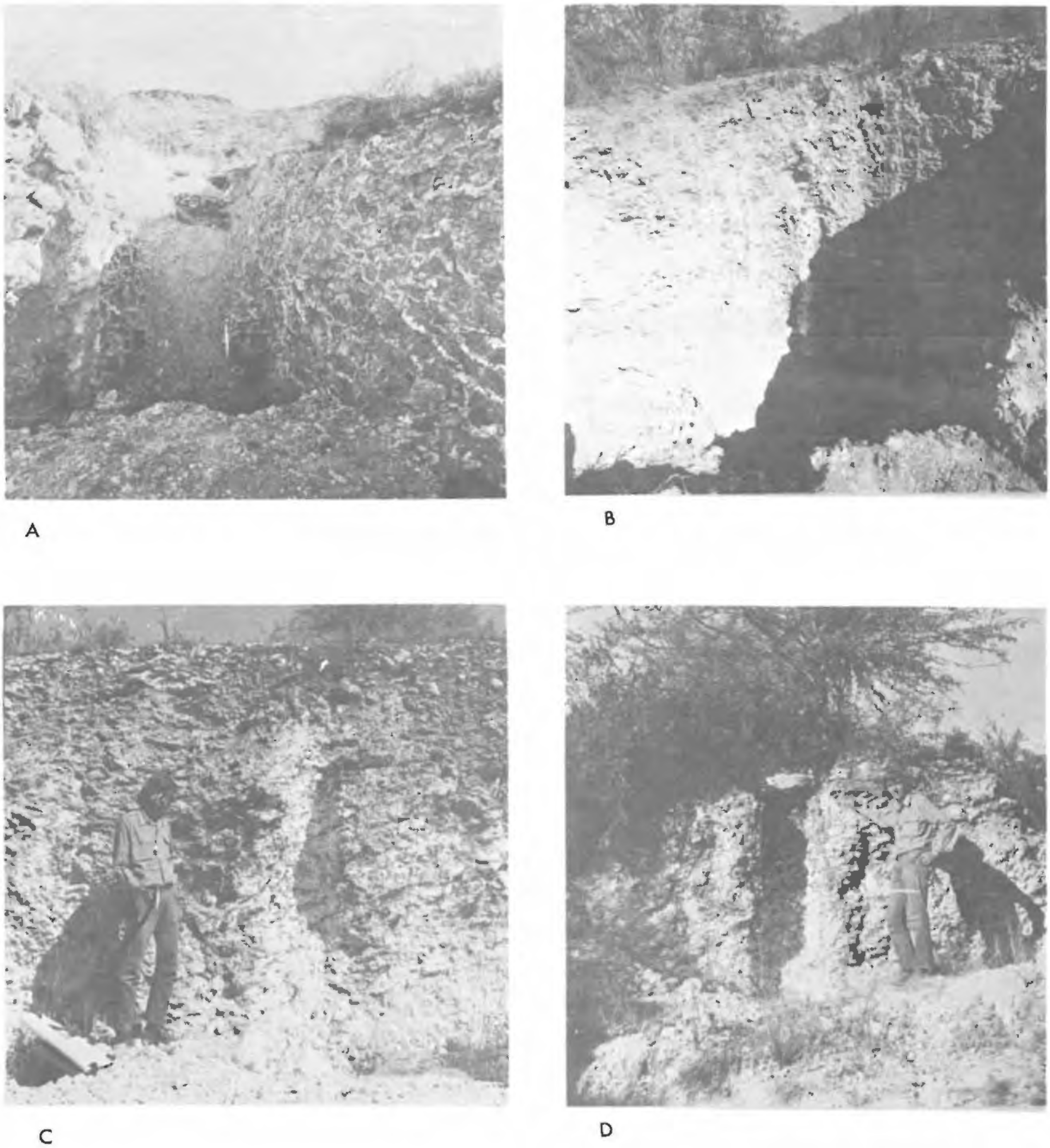

PLATE 1.

A. Skeletal ore in altered pyroxenite.
B. Zebra ore in peridotite, with two vertical magnesite veins to the left of the figure.
C. and D. Massive ore exposed in the quarry faces.

In each case an area next to the figure has been cleaned for the purposes of the photograph. (Photographs by courtesy of Dr. S.A. Hiemstra.)

often occur associated with skeletal and/or zebra ore. The veins vary in width from 2 to 20 cm and generally strike north-south, although wide deviations from this preferred orientation are common. They may display an internal small-scale veining parallel to the strike of the vein as a whole, and in such instances tiny relicts of altered host rock occur between the microveins. Generally, however, the vein ore is relatively clean, the chief impurities being chalcedony or finely crystalline quartz and rare patches of malachite, all of which occur in cavities in the magnesite. The veins may be isolated or they may occur in swarms. Two vertical magnesite veins occur to the left of the figure in Plate 1B. A vertical vein stands out as a prominent feature in Plate 2A.

2.8.4. Nodular ore

Irregularly shaped, highly porous nodules, ranging in size from a few millimeters to several centimeters in diameter are often associated with the above three types. They are generally confined to steep slopes of rather deeply incised drainage channels, where they are almost invariably situated on the steeper undercut slope and die out towards the bottom. The nodules are rather dirty, being associated with much soil and calcrete, and generally contain patches and boulders of weathered host rock. The nodular ore does not exceed 2 meters.

2.8.5. Massive ore

This variety constitutes between 85% and 95% of the magnesite on Arpiesboomen and is the only type which persists

........./ for .....

for more than a few tens of meters along strike. A general view of typical massive ore is shown in Plates 1C, 1D and 2B (in each case a narrow area has been cleaned in the quarry face for the purposes of the photograph). The upper part of the sequence is shown in Plate 3A while Plate 3B is a close-up of the middle part.

The magnesite is often overlain by a layer of so-called blanket reef (VAN ZYL et al. 1942), which varies in thickness from a few cm to about 60 cm. It forms a more or less continuous layer at the surface over most of the deposit situated on gently sloping ground. It is absent in the lower lying flat areas, where the magnesite is overlain by a layer of soil 1 to 2 feet thick. The blanket reef consists of angular fragments of magnesite and rounded pyroxenite boulders set in a hard ferruginous calcrete (Plate 7A).

The blanket reef is generally underlain by a layer of unconsolidated magnesite nodules, averaging about 0.5 m in thickness. The nodules are generally of pebble and small boulder size, highly porous and mixed with considerable amounts of soil and calcrete. A limited number of rounded nodules 5 to 15 cm in diameter and consisting of very clean, compact magnesite are found on the surface. They invariably display well developed colloform and septarian structures, and the latter are commonly filled with red-brown calcrete. (Plates 7B, 7C and 7D.) Pebbles and boulders of scree are concentrated on or near the surface, but are scattered throughout the magnesite down to a depth of at least 8 m below surface. Norite boulders predominate at the surface, but die

......../ out .....

A.

Prominent vertical magnesite vein.

PLATE 2.

B.

Typical massive ore with blanket reef at the surface, passing downwards into soil-contaminated nodular ore and finally clean magnesite.

PLATE 3.

A.

Detail of upper part of massive ore profile.

B.

Detail of middle part of profile showing the distribution of pockets and encrustaceons of impure material through the magnesite nodules.

out in depth, while the pyroxenite boulders show little variation with depth.

At a depth of between 1 and 2 m from the surface the magnesite consists of boulders ranging in size from 2 or 3 cm to a foot in diameter; most commonly they are about the size of a fist. The boulders are usually not completely separated from one another, but form a semi-continuous zone with irregularly shaped cracks and cavities. The magnesite is generally porous but may be very hard and dense. A very crude horizontal or gently dipping stratification is visible in places (Plate 1C). Impurities are contained in the pockets and cracks in the magnesite : these consist largely of encrustaceans of pale grey to brown dolomite, quartz and calcite, clusters of magnetite and chromite grains, a light red-brown clay and minor quantities of orthopyroxene and feldspar grains. Soil is concentrated at the surface, but decreases with depth and becomes insignificant at about 2 m below the surface.

Information regarding the composition of the ore below a depth of 2 to 3 metres is scant; only two shafts of any significant depth have been dug in the massive ore : one 7 m deep at Locality V (Shaft A) and the other 7,9 m deep at Locality XV (Shaft B). Both ended in good massive ore and indicate that the ore improves slightly with depth, although nowhere do the impurities disappear altogether.

On the basis of 88 wagon-drill holes sunk between 1970 and 1972 Goldfields of S.A. Ltd., delineated three flat-lying ore bodies. These are shown on the map. The average thickness of the ore is 4 metres, but may reach

........./ 10 .....

10 metres in places.

2.8.6. Distribution of the ore

The skeletal, zebra, vein and nodular ores are invariably closely associated and they occur in an environment which is quite distinct from that in which the massive ore is found : the former environment has been marked 'B' on the map, while areas underlain by massive ore have been marked 'A'. To the east of the westernmost fault these two environments lie close together, but to the west of this fault they are generally widely separated.

Environment B is situated immediately above the foot of the hill slope and in any one locality the outcrop never covers more than a few hundred square meters. The magnesite found in this environment is apparently subject to strict stratigraphic control, occurring sporadically in an horizon which runs parallel to the strike of the igneous rocks and which is markedly displaced by the westernmost fault.

The massive ore, on the other hand, invariably occurs to the north of environment B and is situated on gently sloping or flat ground. It is apparently not strata-bound, the strike of the outcrop being unaffected by any of the faults. An elongate body of massive ore running discontinuously between drainage channels in an east-west direction can be traced over a total distance of 6 km.

three

mineralogy

3.1. Introduction

For the purposes of the mineralogical study it is convenient to divide the sampled material into four classes. After removing the impurities adhering to the surfaces of the magnesite nodules the cobbed ore and impure material were analysed separately. The host rocks are classified as slight to moderately altered or strongly altered on a basis of their amenability to conventional slide cutting procedure. Thus, the four classes analysed are : cobbed magnesite, impurities removed by cobbing, slight to moderately altered host rock and strongly altered host rock.

............/ 3.2. .....

3.2. Cobbed magnesite

The field positions of the cobbed magnesite samples are labelled from 1 to 19 on the attached geological map. Sample 11 represents a nodule of clean magnesite lying on the surface. Samples 1 and 17 were taken from magnesite veins at localities I and XV respectively : the latter vein is shown in Plate 1B. The remaining samples are representative of the Massive ore described in Section 2.8.5. The depth from the surface at which the samples were taken is shown in Table IV. Samples 2 to 8 and 13 - 14 were collected in two prospecting shafts labelled A and B respectively.

3.2.1. Chemistry

After crushing to -120 mesh the samples were taken into solution in 5N HCl and analysed for MgO, CaO, MnO and Fe_2O_3 by atomic absorption spectrometry. These results, together with figures for the loss on ignition and insoluble residue, are summarised in Table III.

Three samples of uncobbed massive ore (samples 20-22), analysed by the NIM laboratories, are given in Table IV. A comparison of these results with those shown in Table IV indicates the upgrading effect achieved by cobbing the ore.

3.2.2. Carbonate mineralogy

3.2.2.1. Magnesite-dolomite ratios

X-ray diffraction traces revealed the presence of varying amounts of dolomite in the cobbed magnesite samples. A modified form of

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TABLE III.

Chemical and mineralogical composition of cobbed magnesite.

Sample	MgO	CaO	MnO	Fe_2O_3	Insol.	L.O.I.	Total	Dolomite			Depth (feet)	
								Meas.	Calc.	Diff.		
1	46,20	1,05	-	-	1,80	51,08	100,14	BDL	3,6	-3,6	0	V.O.
2	43,20	4,50	-	0,01	2,78	49,77	100,26	16,0	15,8	+0,2	4	M.O.
3	46,20	1,25	-	0,04	1,09	51,40	99,98	BDL	4,4	-4,4	5	M.O.
4	46,60	2,20	-	0,01	1,03	50,28	100,12	7,0	7,7	-0,7	8	M.O.
5	36,90	8,80	-	0,04	6,50	47,59	99,83	31,4	30,7	+0,7	12	M.O.
6	46,30	2,70	-	0,01	0,41	50,99	100,41	8,6	9,5	-0,9	16	M.O.
7	45,70	1,40	-	0,01	2,45	50,25	99,81	BDL	4,9	-4,9	18	M.O.
8	42,40	3,90	-	0,01	3,80	49,80	99,91	12,5	13,7	-1,2	20	M.O.
9	45,50	1,00	-	0,01	4,31	49,41	100,23	4,5	3,5	+1,0	5	M.O.
10	40,50	7,50	-	0,02	2,82	48,84	99,68	28,8	26,3	+2,5	5	M.O.
11	43,90	2,10	-	0,ol	5,02	48,82	99,85	BDL	7,4	-7,4	0	S.N.
12	43,50	3,75	-	0,01	2,51	49,75	99,52	14,2	13,2	+1,0	10	M.O.
13	42,40	3,25	-	0,03	6,41	47,57	99,66	11,5	11,4	+0,1	23	M.O.
14	41,50	2,90	-	0,02	6,81	48,38	99,61	8,8	10,2	-1,4	26	M.O.
15	45,20	0,55	-	0,01	5,15	49,03	99,94	BDL	1,9	-1,9	4	M.O.
16	35,40	10,88	0,02	0,02	5,33	48.14	99,79	47,2	38,3	+8,9	6	M.O.
17	43,80	1,10	0,01	0,01	5,94	48,99	99,85	BDL	3,9	-3,9	15	V.O.
18	46,60	1,40	-	0,01	1,11	50,94	100,06	1,3	4,9	-3,5	8	M.O.
19	43,10	4,75	-	0,01	1,74	49,91	99,51	18,0	16,7	+1,3	4	M.O.

KEY:

M.O.:	Massive
V.O.:	Vein
S.N.:	Surface nodule
L.O.I.:	Loss on ignition.
B.D.L.:	Below detection limit.

The field locality of each sample is shown on the map.

TABLE IV.

Chemical analyses of uncobbed magnesite.[+]

Sample	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	TiO_2	Cr_2O_3	MnO	P_2O_5	CO_2	L.O.I.	Total
20	3,11	0,25	4,92	42,19	0,46	0,00	0,00	0,00	0,00	0,00	47,7	49,14	100,07
21	8,58	0,41	9,92	35,63	0,68	0,01	0,01	0,01	0,01	0,00	41,6	45,39	100,65
22	3,32	0,12	8,01	39,91	0,38	0,01	0,00	0,00	0,00	0,02	47,0	48,26	100,03

[+] Analyses by NIM Analytical Division.
Samples all represent uncobbed massive ore. Field positions shown on map.

the X-ray diffraction technique used by WEBER and SMITH (1961) to determine calcite-dolomite ratios in carbonate rocks was used to measure quantitatively the proportions of magnesite and dolomite. This method consists of measuring the diffracted X-ray intensities of the most intense diffraction peaks for magnesite and dolomite in a series of mixes of known proportions and plotting the results graphically; the intensity ratios for the samples of unknown composition are then measured and the proportions of the carbonates obtained by interpolation from the calibration curve.

The dolomite used in the calibration of the standard curve was supplied by the Bureau of Analysed Standards (U.K.), who guarantee 98,1% $CaMg(CO_3)_2$, and sample 15 was used as the magnesite standard. Corrections for impurities were applied in both cases : the CaO in the latter (0,55%) was assumed to enter into dolomite.

The d_{104} peak was measured for both minerals. For cobalt radiation this is situated at $36,3^{\circ}$ for dolomite and $38,1^{\circ}$ for magnesite. The intensities were determined by summation of the gamma-ray counts from $35,7^{\circ}$ to $36,7^{\circ}$ and from $37,6^{\circ}$ to $38,6^{\circ}$ respectively, and correcting for the background, measured between 39° and 40°. The intensity ratio for each of the standard mixes was measured 10 times and the means plotted as weight per cent dolomite against Intensity dolomite / Intensity dolomite + Intensity magnesite. Fig. 5

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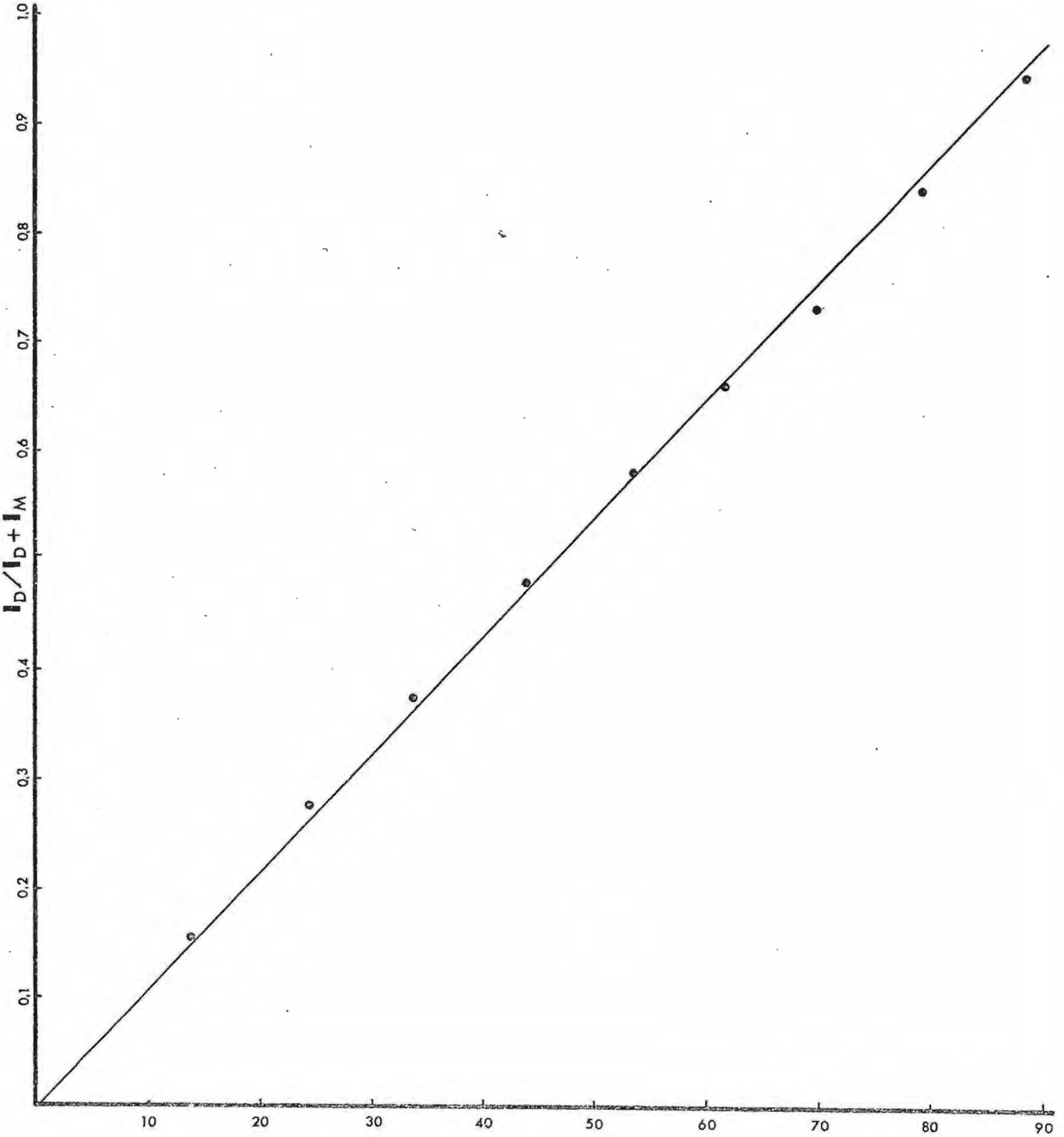

FIGURE 5 :

Diagram for the estimation of the composition of magnesite-dolomite mixtures from the relative intensities of the d_{104} diffraction peaks.

the best fit to these points obtained by the method of least squares.

WEBER and SMITH (op.cit.) showed that for dolomite-calcite mixtures the measurements are free from interference from quartz, magnetite, hematite and clay minerals. These authors evaluated the standard deviation for a duplicate analysis as 1,30 weight per cent.

The weight per cent dolomite in the cobbed magnesite samples as determined by the above method is shown in Table III. These results are compared with the calculated dolomite content - obtained by assuming that all the CaO enters into dolomite - and a good correlation found for most of the samples within the limits of experimental error. The notation BDL in Table III indicates that, although the presence of dolomite was shown on the X-ray trace of the sample, the quantity lies below the detection limit of the modified Weber and Smith method. This is most probably due to a systematic overestimation of the background value of the gamma count. A series of runs containing between 1 and 5% dolomite showed that the lower detection limit lies in the vicinity of 3,5 to 4 weight per cent dolomite.

For those samples whose measured dolomite content is significantly lower than the calculated quantity, it is suggested that some of the CaO may be within some other Ca-rich phase such as

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calcite, aragonite or huntite. X-ray traces showed no signs of any of these minerals, nor of hydromagnesite, nesquehonite, lansfordite or brucite, although it seems likely that, if present, these phases would occur in undetectably small quantities.

$MgCO_3$ enrichment relative to the normal stoichiometric proportions for dolomite is the only tenable explanation for those samples in which the measured dolomite content is significantly greater than the calculated figure. This hypothesis was tested by calculating the $CaCO_3$ content of seven dolomite samples (See Section 3.2.2.2.), all of which were found to contain less than 50 mole per cent $CaCO_3$ (See Table V).

3.2.2.2. Cell dimensions and composition of the individual carbonates

The cell dimensions of 9 magnesites and the coexisting dolomites of 7 of these were determined by measuring the 12 most prominent reflections on an X-ray diffractometer using quartz as an internal standard, and then calculating d, a_o and C_o by means of a computer programme drawn up by APPLEMAN and EVANS The programmes were run by the NIM.

The $CaCO_3$ content of each sample was determined using the curves established by GOLDSMITH and GRAF (1958) relating the lattice constants to the chemical composition. These authors estimate a possible 2% error inherent in the method. It is

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justifiable to assume a linear relationship between the cell sizes and $CaCO_3$ content for the Aapiesboomen samples as the chemical analyses show negligible amounts of MnO and Fe_2O_3 (See Table III). The results (Table V shows that the dolomites contain between 43,1% and 46,2% $CaCO_3$ and that $CaCO_3$ solid solution in the magnesites does not exceed 1%.

3.2.2.3. Staining techniques

In order to determine the habit of the dolomite and to verify the presence or absence of calcite and/or aragonite the staining scheme first proposed by FRIEDMAN (1959) and later extended by WARNE (1962) was utilised. Neither calcite nor aragonite were detected and it appears that the dolomite occurs as cryptocrystalline grains distributed uniformly throughout the magnesite.

3.2.3. Insoluble residue

After careful hand cobbing to remove any obvious foreign material the magnesite nodules still contain impurities disseminated through the carbonate : this is the fraction determined as 'insoluble' in Table III. Since this material is generally present in quantities which lie below the lower detection limit of normal X-ray diffraction methods, it was first separated by crushing to -120 mesh and standing in a 0,1M solution of HCl until virtually all the carbonate had dissolved.OSTROM (1961) has shown that even the most sensitive clay minerals are unaffected by 0,1MHCl, provided that some carbonate is always present. The insoluble residue was

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found to consist mainly of clay with a minor silt fraction (between 0 and 20%).

The clay was identified as palygorskite by the method recommended by CARROLL (1970a). This involves disaggregation of the clay by agitating with a suitable deflocculating agent, settling the -2 micron fraction onto a glass slide and then subjecting it to X-ray diffractometry.

Quartz constitutes on average approximately 90% of the silt fraction. The grains may be clear or stained and frequently contain numerous inclusions. Opaque, black grains are the next most abundant, magnetite being the most common with lesser amounts of chromite. Orthopyroxene, highly weathered labradorite and phlogopite, and apatite occur as accessories.

3.2.4. Textures

The magnesite is cryptocrystalline and generally porous. The pores range in size from the tiniest 'holes' visible only under the microscope to openings up to 1 mm across and may constitute up to 10 or 20% of the volume of the ore.

The habit of the carbonate was studied by means of the scanning electron microscope. Typical surface features are shown in Plates 4A-D. It seems likely that the well defined crystal habit seen in Plates 4A and 4B was produced by cleavage during sampling and that the characteristic habit is that shown in Plates 4C and 4D.

Clusters of magnetite and clay particles up to 1

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TABLE V.

Lattice dimensions (Å) and $CaCO_3$ content (mole per cent) of magnesites and dolomites. [+]

Sample	Magnesite			Dolomite		
No.	Ao	Co	%$CaCO_3$	Ao	Co	%$CaCO_3$
2	4,6331	15,011	0,0	4,7961	15,956	46,2
5	4,6367	15,043	1,0	4,7974	15,961	46,2
8	4,6345	15,030	0,3	4,7993	15,971	46,0
10	4,6337	15,019	0,1	4,7928	15,913	44,8
13	4,6342	15,013	0,2	4,7967	15,947	43,3
14	4,6308	15,017	0,0	4,7944	15,960	45,3
15	4,6363	15,009	0,9			
16	4,6321	15,019	0,0	4,7904	15,924	43,1
17	4,6370	15,024	1,1			

[+] Cell dimensions obtained by least squares method of APPLEMAN and EVANS. Per cent $CaCO_3$ deduced using data of GOLDSMITH and GRAF (1958).

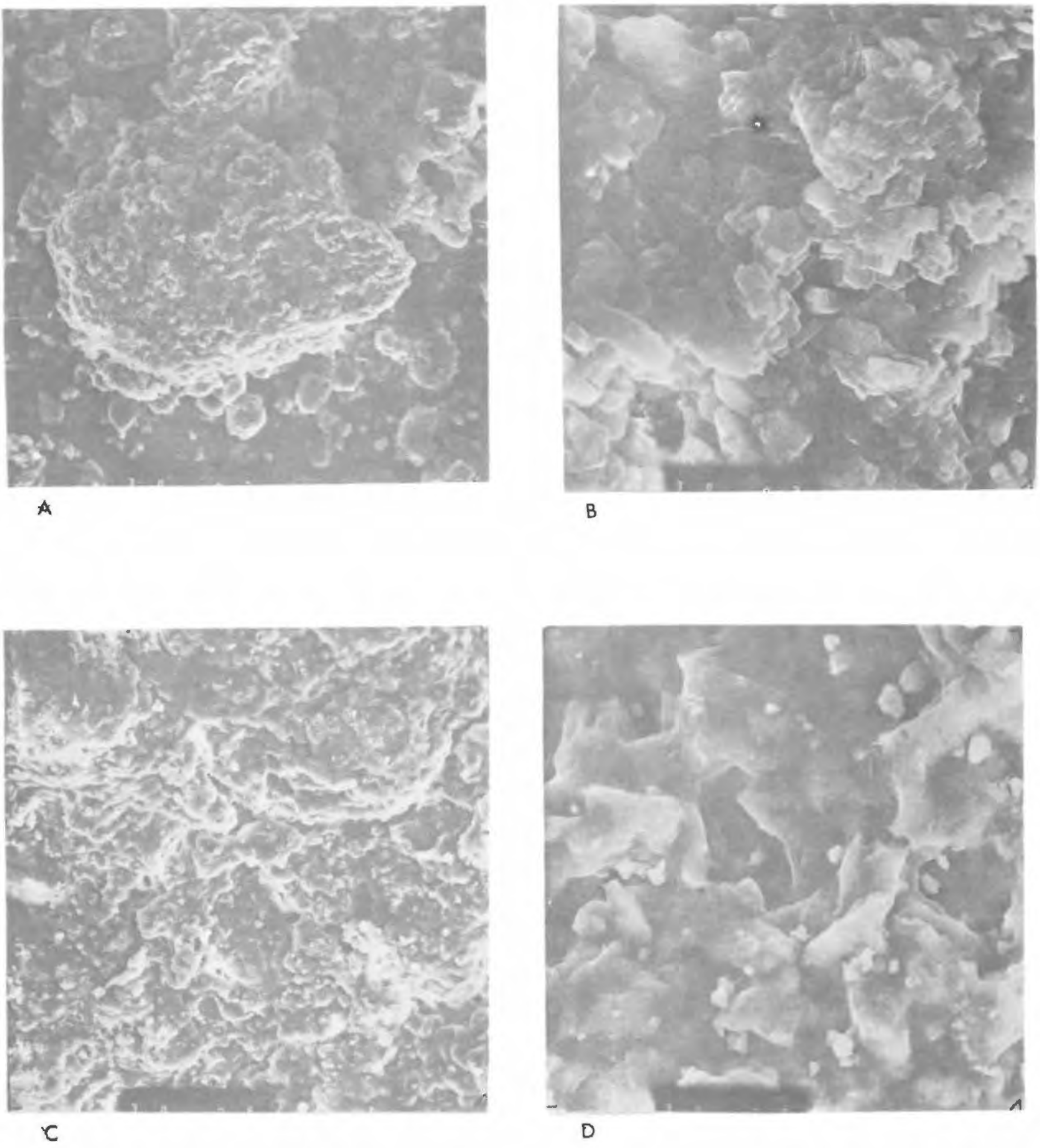

PLATE 4.

Surface textures of the massive ore as viewed under the scanning electron microscope. B(X4500) and D(X750) are enlargements of A(X525) and C(X225) respectively. (Photographs by Mr. R. Cross of the Electron Microscopy Unit, Rhodes University.)

or 2 mm in diameter are sometimes visible to the naked eye. Small pebbles of weathered pyroxenite are less common. The silicates and oxides are usually distributed uniformly through the carbonate. Microscopic examination shows the largest grains comprising the silt fraction to measure 0,5 mm across; these are rare, however, the most common size being less than 0,06 mm. Magnetite and chromite are the only minerals other than quartz which attain diameters greater than 0,13 mm.

3.3. Impurities removed by cobbing

The impure material occurring as films, veins and lenses surrounding the magnesite nodules was investigated by the same techniques outlined in Section 3.2. After crushing and dissolving the carbonate in 0,1M HCl and separating the -2 micron clay fraction by deflocculation and differential settling, the components of the remaining insoluble material were separated by means of a Haultain super panner and examined under the microscope. A typical analysis is given below :

Clay : 18,0% (by weight)
Light silt : 0,3%
Heavy silt : 0,2%
Carbonate : 81.5% (by difference).

The clay was identified as palygorskite by X-ray diffractometry and its habit found to be fibrous when viewed under the electron transmission microscope (See Plate 5A). A chemical analysis of one palygorskite sample is given in Table VIII together with a computation of the number of constituent ions on the basis of 26 oxygens. The results may be compared with palygorskite analyses

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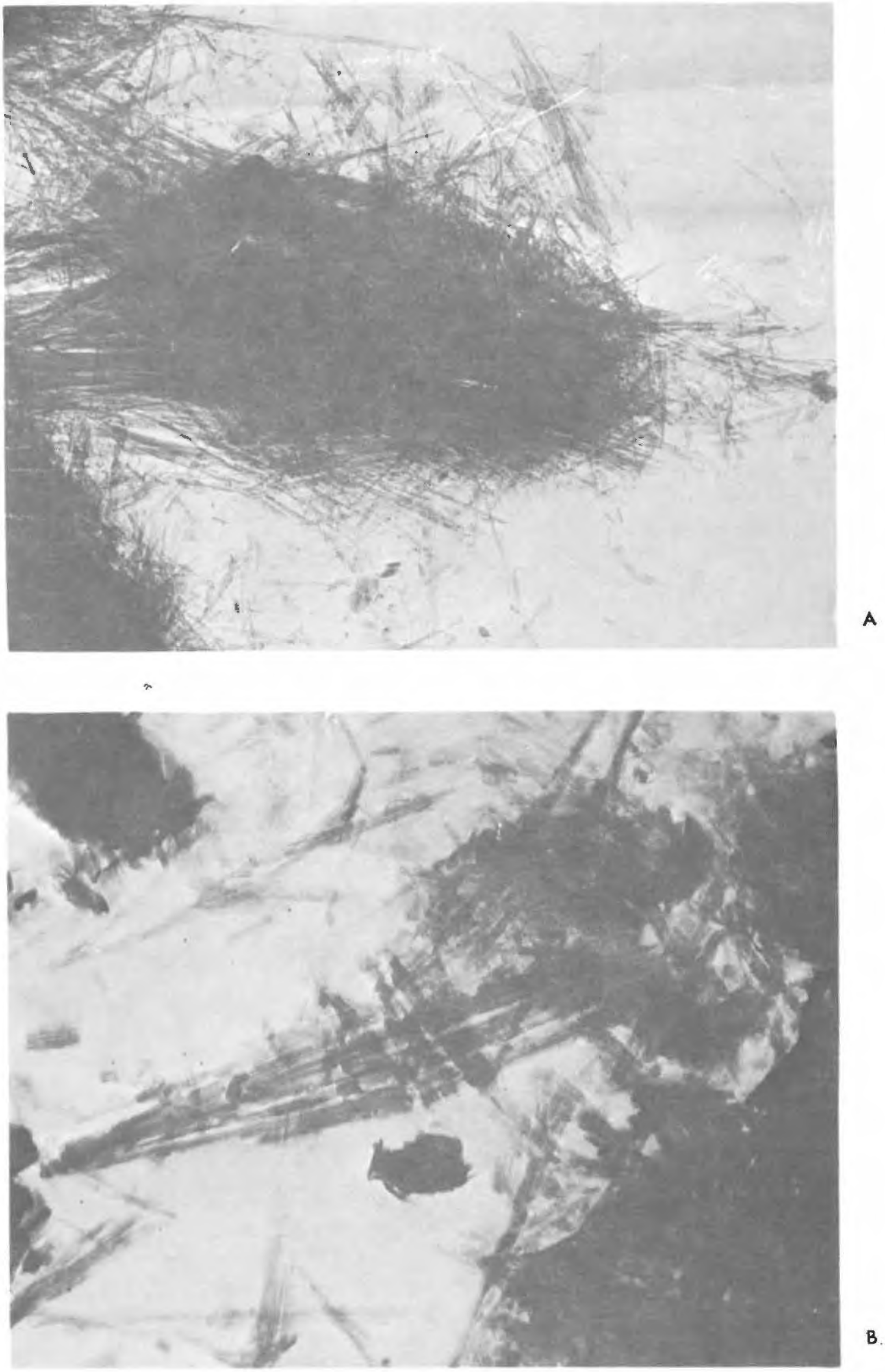

PLATE 5.

Transmission electron photomicrographs of : A, palygorskite (X26 400) and B, hornblende (X55 000).

(Photographs by courtesy of Mr. R. Cross, Electron Microscopy Unit, Rhodes University.)

quoted by CAILLERE and HENIN (1961) : the main differences displayed by the Aapiesboomen clay are a fractionally lower Al content, slightly higher Mg and Fe content and a lesser water content. It is unlikely that these differences are a result of the acid treatment, since NATHAN (1968) has shown that whereas Mg is preferentially removed in acid solution, this effect only becomes noticeable at elevated temperatures and/or under strongly acid conditions. A more realistic explanation is that the clay fraction contains small quantities of foreign material.

The light silt fraction was found to contain approximately 65% quartz, 25% orthopyroxene, 5% labradorite, 5% clinopyroxene and accessory apatite. Magnetite constitutes approximately 75% of the heavier fraction, with chromite accounting for the remainder.

X-ray diffraction methods indicate that the carbonate consists of magnesite and dolomite in the ration of approximately 3 : 1, with traces of calcite.

Microscopic and staining techniques applied to the uncrushed material show that all the constituents are intimately intergrown. Quartz, dolomite, magnesite and calcite are sometimes present as surface encrustaceans, films and veins, suggesting that these minerals are precipitated contemporaneously with the deposition of clay and silt in openings between the magnesite nodules.

3.4. Slightly to moderately altered host rock

3.4.1. Introduction

Thin sections were cut of specimens of host rock containing slight to moderate amounts of carbonate (samples P4 to P8). Sample P4 represents an original peridotite and

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the remainder were derived from pyroxenites. In order to obtain as complete a sequence of the alteration processes as possible, one sample of unaltered peridotite (P3) and two of pyroxenite (P1 and P2) were also examined.

3.4.2. Mineral composition and textures

Modal analyses of the 9 samples were carried out by point counting and the significance of the results tested by Bayly's method (BAYLY, 1965). This method distinguishes two possible sources of error (apart from that due to incorrect identification) : one resulting from unrepresentative sampling (Vs), and the other from a statistical bias in the counting procedure (Vc). Vs and Vc are calculated as follows :

$$Vs = \frac{132i^2p}{A}$$

$$Vc = \frac{p\ (100-p)}{n}$$

where i = mean intercept cut off on the relevant mineral

p = estimated percentage of mineral present

A = sample area

n = number of points counted.

Vc and Vs are then combined as follows to give the standard deviation, S :

$$S = \sqrt{(Vc = Vs)}$$

The results of the analyses are given in Table VI.

The mineralogical compositions of both the peridotites and pyroxenites are highly variable. For example, P4 contains

........../a .....

TABLE VI.

Modal analyses of slightly to moderately altered host rock.

	P1(A)		P2(A)		P3(B)		P4(C)		P5(D)		P6(D)		P7(D)		P8(D)		P9(D)	
	%	S	%	S	%	S	%	S	%	S	%	S	%	S	%	S	%	S
Carbonite	–		–		0,1		4,4	1,8	–		0,1		0,7	1,7	16,7	2,4	24,0	1,4
Orthopyroxene	82,6	1,1	89,6	1,3	17,4	1,1	34,9	2,2	93,2	1,1	72,8	1,5	51,1	2,8	28,2	1,9	60,7	1,8
Clinopyroxene	7,2	1,4	5,1	2,1	1,6	1,2	–		1,1	1,0	17,9	2,4	22,4	1,8	16,7	1,8	6,4	2,0
Feldspar	9,6	1,9	4,2	1,7	12,9	1,2	3,4	1,9	4,3	1,5	9,0	1,8	24,2	1,5	35,9	2,2	7,6	1,6
Olivine	–		–		14,3	1,1	17,8	1,3	–		–		–		–		–	
Serpentine	–		–		44,4	1,0	36,9	1,5	–		–		–		–		–	
Magnetite	0,5	1,8	1,1	1,9	9,0	1,1	2,4	1,8	1,0	1,2	–		1,5	1,6	–		0,1	
Phologopite	0,1		o,1		o,1		–		0,1		–		0,1		0,5	1,9	1,2	1,1

A: Unaltered pyroxenite
B: Serpentinised peridotite
C: Carbonate-bearing peridotite
D: Carbonate-bearing pyroxenites.

Positions of samples shown on map.

a quarter as much feldspar as P3 and twice as much pyroxene; the feldspar content of the pyroxenites varies from 3,4% to 35,9% and the total pyroxene content from 44,9% to 94,7%.

The olivine is intensely serpentinised, and, in the case of P4 extensively stained by an amorphous red-brown iron oxide (See Plate 6A). The X-ray method of YODER and SAHAMA (1957) was used to determine the composition of the olivine : P3 was found to contain 91 mole per cent forsterite and P4 84%.

The serpentine was identified as chrysotile according to the X-ray criteria recommended by WHITTAKER and ZUSSMAN (1956). It occurs as veinlets in and around the olivine and is intimately associated with numerous small grains of magnesite.

Labradorite occurs as interstitial grains in both the peridotites and pyroxenites. It is rarely unaltered and in the more extensively altered rocks it is strongly saussuritised.

The orthopyroxene is invariably bronzite ($2V_\gamma = 75^\circ - 90^\circ$) displaying fine lamellac and blebs of exsolved augite. Bronzite is frequently altered along fractures to a fine-grained indeterminate material displaying a high birefringence (See Plate 6B). Clinopyroxene occurs as intercumulus crystals of augite ($2V_\gamma = 40^\circ-45^\circ$). Both the bronzite and augite are cut by stringers and veins of carbonate (See Plate 6C).

The carbonate consists essentially of dolomite with

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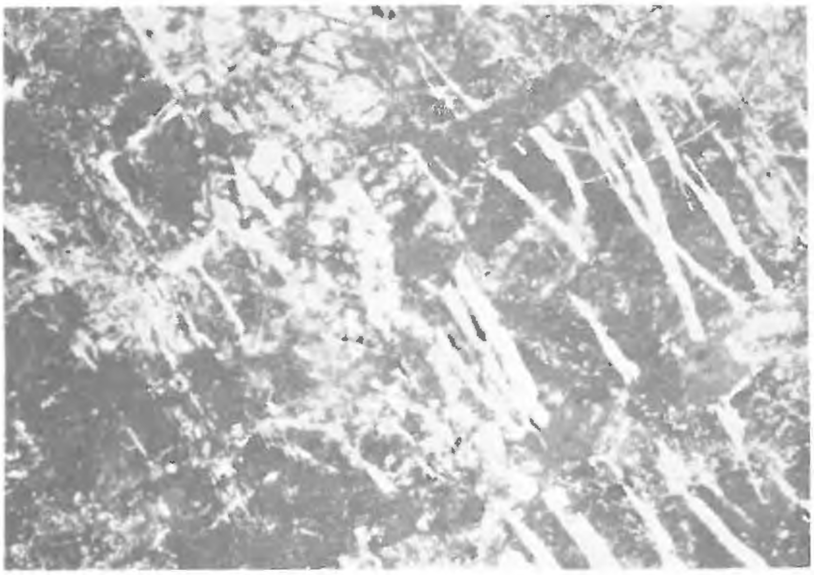
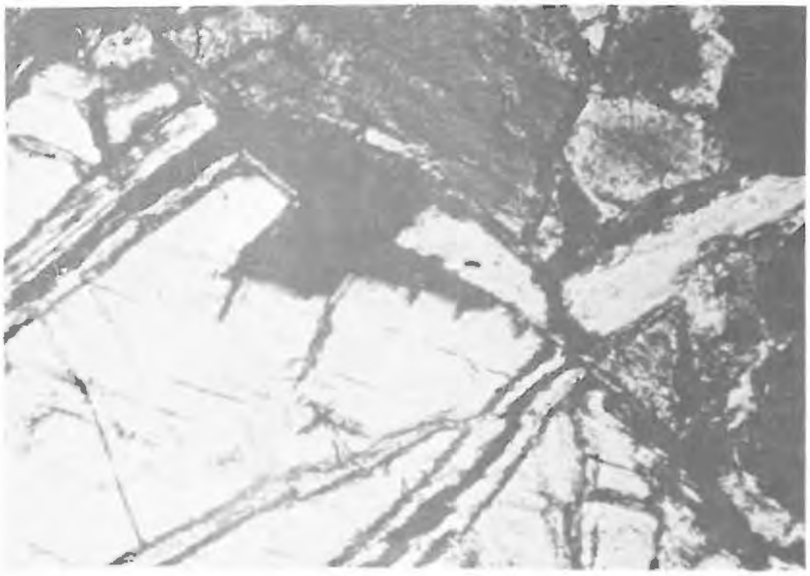


A.

Serpentinized peridotite, with chrysotile veins cutting intensely stained olivine.

B.

Pyroxenite showing incipient alteration of pyroxene along fractures and two carbonate grains at middle right.



C.

Pyroxenite in which the pyroxene grains are veined and surrounded by a fine-grained quartz-carbonate intergrowth.

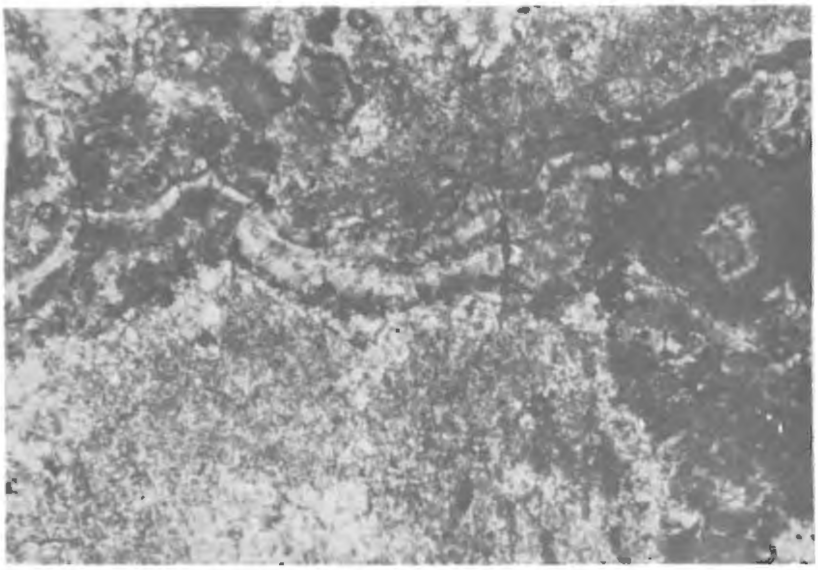
PLATE 6 (a)

D.

← Phlogopite surrounded by quartz-carbonate.

E.

Quartz-carbonate with elongate phlogopite → grains at upper centre.



F.

Quartz-carbonate intergrowth displaying colloform banding.

PLATE 6 (b)

minor magnesite and is frequently intergrown with phlogopite and quartz (See Plates 6D and 6E). It may occur as small aggregates in cavities in the rocks (See Plate 6B), as vein fillings (See Plate 6C), or as large masses, where it may be massive or display colloform banding (See Plate 6F). Phlogopite appears as both a primary and a secondary mineral in the peridotites, but only as an alteration product in the pyroxenites. In the former habit it occurs as intercumulus grains showing no signs of alteration, while the secondary phlogopite grains are smaller, generally have a hazy appearance and are invariably associated with carbonate.

3.5. Strongly altered host rocks

3.5.1. Introduction

Because of their friable nature and tendency to disaggregate rapidly on contact with water, thin sections of these samples could not be cut. The following scheme was thus adopted :

(a) each sample was crushed to - 120 mesh, sieved into two fractions - 120-200 mesh and - 200 mesh - mounted in balsam, polished with abrasive powder in paraffin, and modal analyses carried out by point counting;

(b) the carbonate was then dissolved using 0,1M HCl and the clay fraction identified by the method described under Section 3.2.3; and

(c) finally, the carbonate fraction was investigated by X-ray techniques.

.........../ 3.5.2. ......

3.5.2. Modal analysis

The results of the modal analyses are tabulated in Table VII (a). It is not necessary to quote the modal composition of each grade size separately as the two do not differ. The standard deviations, S, listed in Table VII (a) are taken as the square root of Bayly's counting variance, Vc, since the crushing and quartering of the sample before mounting would eliminate any error due to unrepresentative sampling.

The material listed as 'clay + carbonate' consists of an intergrowth of carbonate and clay-sized material with minor, very fine-grained serpentine and quartz. Both of the latter occur also as larger grains, frequently associated with each other and with the clay-carbonate intergrowths. The larger quartz grains commonly exhibit undulose extinction and colloform banding. The serpentine was identified as chrysotile by the X-ray method described in Section 3.4.2.

3.5.3. Acid solution

After crushing, the samples were allowed to stand in 0,1M HCl with periodic stirring until effervescence ceased. The carbonate content was taken as the weight loss and the clay fraction calculated by subtracting this figure from the 'clay + carbonate'value in Table VII (a). These results are shown in Table VII (b).

The clay fraction remaining after solution of the carbonate was found to be amorphous. It was surmised that the crystal structure may have been destroyed by the

........../prolonged ......

TABLE VII.

Mineral content of strongly altered host rocks.

(a) Modal analyses by point counting.

	P10(E)		P11(C)		P12(E)		P13(E)		P14(E)		P15(E)		P16(E)		P17(E)	
	%	S	%	S	%	S	%	S	%	S	%	S	%	S	%	S
Pyroxene	17,1	2,5	5,0	2,8	>1		>1		1,3	2,4	>1		3,4	3,0	>1	
Serpentine	13,0	2,6	8,5	2,7	10,6	2,6	5,9	2,3	3,2	2,4	2,7	2,7	2,1	3,0	2,2	2,1
Clay + carbonate	67,1	1,6	85,3	1,1	88,5	1,3	92,8	0,6	93,6	0,6	94,7	1,5	93,5	0,8	97,3	0,9
Magnetite	2,8	2,8	>1		>1		>1		–		>1		>1		–	
Phlogopite	–		–		>1		>1		–		>1		>1		–	
Brugnatellite	–		–		–		–		–		>1		>1		–	
Quarty	–		–		>1		–		–		–		>1		–	

Clay and carbonate proportions by acid solution. (Weight per cent).

(b)

Carbonate	31,4	61,4	82,3	82,6	62,7	62,8	89,3	86,9
Clay	35,7	23,9	6,2	10,2	30,9	31,9	4,2	10,4

(c) Carbonate composition by X-ray diffractometry. (Weight per cent).

Magnesite	31,4	–	–	–	–	53,8	–	70,0
Dolomite	BDL	61,4	82,3	82,6	62,7	9,0	89,3	16,9
Calcite	BDL	–	–	–	–	–	–	–

C: Carbonated bearing peridotite

E: Rock type not obvious because of strongly altered nature.

Positions of samples shown on map.

prolonged acid treatment, and the -2 micron fraction was therefore separated from a fresh batch of samples by deflocculation, differential settling and treatment with 0,1M HCl for only 12 hours to remove the carbonate. All eight samples thus isolated were found to display X-ray patterns characteristic of amphiboles and to exhibit fibrous habits when examined under the electron microscope (See Plate 5B).

Since all the fibrous amphiboles possess very similar X-ray patterns, silicate analyses were performed on three of the samples in order to identify the species. The results, listed in Table VIII show all the samples to be hornblendes. LEAKE (1968) lists the following criteria for distinguishing a 'superior' amphibole analysis :

(a) The Si + Al in the half-unit cell must not be less than 7,92.

(b) The sum of Ca + Na + K must lie between 1,75 and 3,05.

(c) The sum of $Al^{VI} + Fe^{3+} + Fe^{2+}$ + Mn + Mg + Cr + Ni must lie between 4,75 and 5,25.

(d) The sum of OH + F + Cl should lie between 1,00 and 2,99.

All three analyses shown in Table VIII fall short of at least two of these conditions : this may be due to either a partial dissolution of the minerals during the acid treatment or the presence of impurities, or both. The summation of the four analyses lie between 99,6 and 100,4 per cent, suggesting that the analytical techniques have not

........../ introduced .....

TABLE VIII.

Chemical analyses of three hornblendes and one palygorskite.

	P10[*]	P12[*]	P14[*]	3[+]
SiO_2	48,81	46,83	47,29	51,61
Al_2O_3	2,25	0,46	1,26	6,64
Fe_2O_3	12,14	4,76	9,31	6,26
MgO	21,45	22,10	17,75	23,90
CaO	1,15	15,75	6,20	0,92
Na_2O	1,00	0,06	1,11	–
K_2O	–	–	0,80	–
H_2O^+	2,31	2,65	2,91	8,04
H_2O^-	10,67	7,73	13,00	3,06
Total	99,78	100,34	99,63	100,43

	No. of ions on the basis of 24 oxygens.							No. of ions on the basis of 26 oxygens.
Si	7,83		8,00	7,08	7,16	7,47	7,70	6,85
Al	0,43	0,17 0,26		0,08		0,23		1,00
Fe^{3+}	1,47		6,88	0,54	5,54	1,11	5,31	0,62
Mg	5,15			5,00		4,20		4,75
Ca	0,20		0,51	2,56	2,58	1,06	1,56	0,13
Na	0,31			0,02		0,35		–
K	–			–		0,15		–
OH	2,48			2,68		3,09		9,84

[*] Hornblende from samples P10, P12 and P14, respectively.

[+] Palygorskite from sample 3.

serious error. The data are of some value, however, in that they provide a very good indication of the proportions of the constituent elements in the minerals. The hornblendes are all rich in Mg, while Ca, Fe and Na are very variable.

3.5.4. Composition of the carbonate

X-ray diffraction traces of the eight samples show that the carbonate fraction of all but three consists solely of dolomite. Samples P15 and P17 contain dolomite and magnesite, and sample P10 contains calcite in addition. The proportions of dolomite and magnesite in P15 and P17 were determined by the method described in Section 3.2.2.1. (Table VII (C)). The dolomite and calcite contents of P10 are below the detection limit of this technique.

3.6. Mineral parageneses

3.6.1. Peridotites

Although the relationships are not clear in Plate 1B, sample 17 is representative of a prominent vein in a peridotite of which P4 is a specimen; the two are separated by a narrow zone from which sample P11 was taken. It is obvious that P11 is an alteration product of P4 and that 17 represents carbonate derived from these rocks and concentrated in a fracture. P4 is itself altered and was probably derived from a peridotite of similar composition to P3.

Judging from the abundance of serpentine in P3 and the textural relationships between the serpentine and

........./magnetite .....

magnetite, it is clear that the alteration of olivine to serpentine and magnetite commenced at an early stage. Carbonate and quartz were produced later. The saussuritization of the feldspar was a slower process commencing during or immediately after the start of the olivine alteration.

Due to their intensely altered condition, it is difficult to deduce the original nature of the strongly altered host rocks. Since they contain serpentine, a mineral not observed in the altered pyroxenites, it seems more likely that they were derived from peridotites. If this is the correct interpretation then the mineral paragenesis of the peridotites is as follows :

olivine + feldspar + pyroxene
↓
serpentine + magnetite + saussurite + limonite
↓
magnesite + quartz + dolomite + calcite
↓
hornblende + phlogopite + brugnatellite

Sample P10 is unusual in that it represents the only rock in which the amphibole content (35,7%) exceeds the carbonate (31,4%) and which contains calcite (See Table VII). In addition, it contains significantly more pyroxene and serpentine than any of the other highly altered parent rocks and the hornblende displays a poorly developed morphology when viewed under the electron microscope. The evidence suggests that P10 represents a relatively early stage in the alteration process and, by corollary, that hornblende and calcite commence crystallization at the same time or very soon after the first appearance of magnesite, dolomite and quartz.

........../ It .....

It seems that dolomite is formed earlier or at a faster rate than magnesite during the initial stages of carbonate production and that magnesite is the dominant phase formed during the later stages. This is shown by the predominance of dolomite over magnesite in most of the altered host rocks and the reversed ratio in the vein ore and carbonate 'skeletons' of the skeletal ore. These conclusions are supported by the general observation that the dolomite / magnesite ratio is larger for the impure material contained in cavities between the nodules of massive magnesite than for the magnesite nodules themselves. The presence of calcite in sample P10 indicates that this mineral is formed in detectable quantities only during the earliest stages.

3.6.2. Pyroxenites

In the case of the carbonate-bearing pyroxenites two possibilities should be considered : either the carbonate represents material derived from elsewhere, or it is a product of in situ alteration of the pyroxene. The occurrence of intimately associated quartz and carbonate in the smallest stringers in the rock and the existence of thin veins of incipient alteration in the pyroxene grains (See Plate 6B) argue in favour of the latter hypothesis.

Unfortunately, no sequence showing the progressive alteration of any one pyroxenite could be found. It seems clear that the quartz-carbonate is derived directly from the pyroxene, accompanied by the crystallization of minor phlogopite. The mineral paragenesis as shown below is thus simpler than that of the peridotites :

........../orthopyroxene .....

orthopyroxene + clinopyroxene + feldspar
↓
magnesite + dolomite + quartz + phlogopite + saussurite.

four

petrochemistry

4.1. Introduction

The 9 slightly to moderately altered host rocks and 8 strongly altered rocks discussed in Chapter 3 were analysed quantitatively for 15 elements by flame photometric, atomic absorption, spectrophtometric and titrimetric methods. The numbers of the ions contained in a standard cell of 160 oxygens were calculated and the results plotted graphically in order to elucidate the chemical changes occurring during the alteration process.

.........../ 4.2. .....

4.2. Analyses

4.2.1. Methods

The following methods were utilised :

SiO_2 : The spectrophotometric method of Shapiro and Brannock as modified by MAXWELL (1968).

Al_2O_3)
P_2O_5) The spectrophotometric method of SHAPIRO and BRANNOCK (1962).

CaO)
MgO)
Fe_2O_3 (total iron)) By atomic absorption spectroscopy following VOLBROTH (1969).
MnO)

TiO_2 : The spectrophotometric method of RIGG and WAGENBAUER (1961).

Na_2O)
K_2O) By flame photometer following MAXWELL (1968).

FeO : Hot-acid decomposition followed by titrimetric determination by $K_2Cr_2O_7$ (Pratt method as modified by MAXWELL, 1968).

H_2O^+)
H_2O^-) Methods described by MAXWELL (1968).

CO_2 : The evolution-absorption method used by SHAPIRO and BRANNOCK (1962, op.cit.).

Cr_2O_3 : The spectrophotometric method of SANDELL (1959).

The results of the analyses are shown in Table IX.

TABLE IX.

Chemical analyses of host rocks.

	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17
Analyst*									NIM						NIM		
SiO_2	55,72	54,86	42,98	44,18	55,02	53,78	52,06	50,36	50,41	45,48	22,62	12,94	12,90	25,16	16,52	7,98	10,13
Al_2O_3	3,79	4,55	5,56	3,39	4,54	3,51	8,53	13,56	4,21	2,24	2,23	0,84	0,96	1,14	0,66	0,38	0,51
CaO	2,68	3,12	3,14	3,08	2,80	2,34	4,08	5,14	4,59	1,14	15,20	22,38	21,88	13,72	1,54	21,44	0,74
MgO	26,95	26,50	30,65	31,10	28,00	28,25	23,30	17,20	25,65	23,05	23,00	21,00	20,90	19,15	37,80	20,75	37,92
FeO	9,35	8,94	4,51	4,51	5,80	4,71	6,88	6,97	6,91	1,58	0,60	–	0,09	–	0,13	0,11	–
Fe_2O_3	0,90	1,22	5,54	5,57	1,28	3,42	1,64	1,18	0,93	9,82	4,12	1,36	2,19	5,05	2,90	1,10	0,74
Na_2O	0,35	0,61	0,62	0,39	0,65	0,41	0,80	0,80	0,31	0,35	0,25	0,11	0,20	0,15	0,10	0,26	0,11
K_2O	0,11	0,09	0,08	0,10	0,15	0,08	0,15	0,13	0,23	0,08	0,11	0,08	0,09	0,06	0,03	0,06	0,07
P_2O_5	0,03	0,03	0,06	0,06	0,19	0,11	0,11	0,07	0,01	0,09	0,03	–	0,02	0,03	0,01	–	0,13
MnO	0,22	0,21	0,17	0,15	0,16	0,18	0,20	0,18	0,16	0,18	0,05	0,07	0,02	0,09	0,05	–	–
Cr_2O_3	0,32	0,36	0,51	1,06	0,72	0,78	1,31	0,17	–	1,01	0,47	0,09	0,44	0,70	0,19	0,09	0,65
CO_2	–	–	0,16	2,26	0,25	0,08	0,13	0,63	4,54	0,58	25,06	38,73	37,45	23,34	32,44	43,49	45,07
TiO_2	0,03	0,02	0,02	0,02	0,02	0,02	0,03	0,02	0,02	0,03	–	–	–	0,01	0,02	–	–
H_2O^+	0,12	0,06	5,25	3,27	0,17	0,43	0,38	0,57	1,42	3,52	4,26	1,54	1,63	3,85	3,21	2,05	1,87
H_2O^-	0,10	0,06	0,84	0,51	0,15	2,78	0,26	3,01	0,52	10,57	2,10	1,95	2,25	7,46	4,03	3,21	2,69
Total	100,67	100,63	100,09	99,65	99,90	100,88	99,86	99,99	99,91	99,72	100,10	101,09	101,02	99,91	99,63	100,92	100,63

*All analyses by the author unless otherwise stated. NIM indicates analyses performed by the General Superintendence Co. S.A. (Pty) Ltd. at the request of the NIM.

Nature and source of samples as for Tables VI and VII.

4.2.2. Standardization of results

A dunite (DTS) from the USGS collection of analyzed standards and a norite (NIM N) from the NIM collection were analyzed together with the samples in order to standardize the methods and to provide some control over the results obtained. In addition, 3 of the analyses performed by the author were duplicated by the NIM analytical section.

NIM N was analyzed in duplicate to indicate the precision of the analyses.

All these data are shown in Table X.

4.3. Chemical changes involved during alteration

4.3.1. General

It is universally accepted that a comparison of the chemical analyses, given in terms of the weight per cent of the oxides, of a suite of metasomatically altered rocks will not yield an accurate description of the chemical changes involved. Early attempts to surmount the problem were based on the assumption that one of the constituents, usually silica or alumina, remained constant during the alteration, but such methods are now considered quite inadequate.

Many alteration processes, such as the replacement of one mineral by another, rock weathering and the changes effected by hot springs are commonly observed to occur

........../ without .....

TABLE X.

Analyses of standard rock samples.

	DTS[*]		NIM N[**]			P4[+]		P11[+]		P14[+]	
	NCT	USGS	NCT	NCT	NIM	NCT	NIM	NCT	NIM	NCT	NIM
SiO_2	40,74	40,45	53,26	53,22	52,43	44,18	44,50	22,62	24,41	25,16	25,58
Al_2O_3	1,08	0,55	17,06	17,06	16,64	3,39	3,19	2,23	1,78	1,14	0,91
CaO	0,10	0,15	11,19	10,93	11,55	3,08	3,22	15,20	14,14	13,72	14,30
MgO	49,75	49,80	6,65	7,10	7,43	31,10	29,92	23,00	22,58	19,15	19,62
FeO						4,51	4,76	0,60	0,79	0,00	0,12
Fe_2O_3						5,57	5,82	4,12	3,71	5,05	5,06
Na_2O	0,04	0,04	2,51	2,53	2,44	0,39	0,24	0,25	0,22	0,15	0,12
K_2O	0,04	0,02	0,29	0,23	0,26	0,10	0,10	0,11	0,13	0,06	0,08
P_2O_5	0,04	0,02	0,08	0,10	0,04	0,06	-0,02	0,03	-0,02	0,03	-0,02
MnO	0,17	0,12	0,19	0,21	0,17	0,15	0,15	0,05	0,05	0,09	0,08
Cr_2O_3	0,59	0,54	0,09	0,19		1,06	1,05	0,47	0,52	0,70	0,80
CO_2						2,26	2,50	25,06	24,06	23,34	23,52
TiO_2	0,02	0,02	0,03	0,03	0,19	0,02	-0,05	0,00	-0,05	0,01	-0,05
H_2O^+						3,27	3,39	4,26	3,93	3,85	3,15
H_2O^-						0,51	0,57	2,10	1,95	7,46	6,23
TOTAL						99,65	99,48	100,10	98,34	99,91	99,64

[*] Sample DTS from U.S.G.S. collection of analysed standards.

[**] Sample NIM N from NIM collection of analysed standards.

[+] Aapiesboomen samples.

NCT: Author

USGS: Average from numerous analysts.

NIM: " " " "

without any appreciable volume change. The constant volume alteration of serpentinite to talc-carbonate rock and to silica-carbonate rock respectively have been described in detail by CHIDESTER (1962, Section 1.4.2.) and by BAILEY and EVERHART (1964, Section 1.4.1.). A commonly used method to deduce chemical changes from chemical analyses, therefore, is to compare equal columes of rock.

BARTH (1948) has recommended the use of a 'standard cell' containing 160 oxygen atoms. Oxygen is used as a reference standard on the assumption that isovolumetric chemical changes occur by a migration and exchange of cations in a medium composed of relatively stationary oxygen ions : the number of oxygen atoms in any given volume is considered to remain constant. It follows that for any two rocks genetically related by a metasomatic alteration process, a comparison of the numbers of the individual cations associated with a given number of oxygen ions will reveal the chemical changes effected by that process. The number of oxygen atoms in the standard cell is chosen as 160 as this is the number with which approximately 100 cations are associated in most silicate rocks.

CHIDESTER (1962) has pointed out that Barth's method is not applicable to rocks whose cell sizes differ significantly, i.e. those containing minerals of widely different equivalent volumes. The equivalent volume of a mineral is defined as the equivalent weight divided by the density. For rocks in which the constituent minerals have significantly different equivalent volumes the use of a 'modified standard cell' to compare volumes of rock of equal and standard size is recommended. The modified standard cell is defined, in general terms, as that volume of rock containing approximately 100 electropositive ions and is based on Barth's standard cell, as modified by the density of the rock.

4.3.2. Method applied to Aapiesboomen rocks

Since the Aapiesboomen host rocks contain minerals whose equivalent volumes vary from 13,69 for magnesite to 22,63 for quartz (figures from CHIDESTER, 1962) it would appear that Chidester's method is more applicable in analysing their chemical relationships than that proposed by Barth. However, any sophisticated elaboration on the general nature of the chemical changes is considered unrealistic in view of the following :

(a) The slightly to moderately altered peridotites and pyroxenites display a wide variation in both their mineralogical and chemical compositions (See Section 3.4.2., Table VI and Section 4.2.1., Table IX), indicating that the starting materials for the various alteration products differ markedly in composition.

(b) No continuous sequence in the progressive alteration of any one peridotite or pyroxenite was sampled systematically.

(c) The minerals of high and low equivalent volumes tend to occur together; for example magnesite (13,69) is usually associated with quartz (22,63)

............/ and ......

and forsterite (14,65) with chrysotile (22,62). The minerals would therefore produce compensatory effects, leaving the cell sizes of the rocks relatively unaffected.

Thus, it seems unlikely that the modifications suggested by Chidester would add any information of any significance to the results obtained by the use of Barth's standard cell method. The numbers of the ions associated with 160 oxygens were calculated without regard to density considerations. The results are listed in Table XI.

4.3.3. Index of alteration

The first problem to be solved before the chemical data can be usefully interpreted is the choice of a suitable index against which the variations of the ions may be measured. The mineralogical evidence indicates that the progressive alteration is accompanied by the carbonation, hydration and oxidation of the rocks, suggesting the use of the number of C atoms, OH atoms, C + OH or the ratio Fe^{2+} / Fe^{3+} as measures of the degree of alteration. Of these, the number of C atoms per standard cell was chosen as the most suitable, since the formation of carbonate commences early in the alteration process, occurs throughout that process and represents the most obvious and pronounced effect of the alteration.

Hornblende occurs only in the strongly altered rocks, while phlogopite, the only hydrous mineral observed in the peridotites and pyroxenites, is present only in

........../ trace ......

TABLE XI.

Numbers of ions on the basis of 160 (O+OH).

	P1	P2	P3	P4	P5	P6	P7	P 8	P9	P10	P11	P12	P13	P14	P15	P16	P17
Si	51,87	51,25	39,39	40,83	50,95	50,62	48,88	47,92	45,84	45,98	19,21	10,59	10,66	22,49	13,55	6,45	7,72
Al	4,18	4,97	6,01	3,74	5,00	3,89	9,44	15,20	4,56	2,71	2,20	0,78	0,98	1,19	0,66	0,38	0,45
Ca	2,65	3,10	3,06	3,03	2,78	2,39	4,10	5,27	4,45	1,25	13,86	19,61	19,40	13,15	1,36	18,55	0,63
Mg	37,48	31,85	41,85	42,42	38,63	36,63	32,58	24,40	34,76	34,71	29,12	25,61	25,75	25,51	46,14	25,00	43,08
Fe^{2+}	7,27	7,00	3,44	3,47	4,50	3,72	5,39	5,55	5,27	1,35	0,40	–	0,05	–	0,09	0,09	–
Fe^{3+}	0,67	0,90	3,83	3,86	0,89	2,44	1,13	0,89	0,65	7,48	2,60	0,88	1,37	3,38	1,79	0,67	0,45
Na	0,78	1,12	1,10	0,66	1,12	0,78	1,46	1,44	0,54	0,64	0,40	0,20	0,30	0,30	0,18	0,38	0,18
K	0,12	0,12	0,12	0,12	0,22	0,10	0,22	0,12	0,22	0,10	0,10	0,10	0,10	0,06	0,04	0,10	0,08
P	0,02	0,02	0,04	0,04	0,11	0,09	0,09	0,07	–	0,11	–	–	0,01	0,02	0,01	–	0,09
Mn	0,17	0,17	0,11	0,11	0,11	0,17	0,17	0,17	0,01	0,16	0,05	0,05	0,01	0,05	0,03	–	–
Cr	0,26	0,23	3,27	0,77	0,55	0,55	1,01	0,11	–	0,76	0,30	0,07	0,29	0,49	0,09	0,06	0,36
C	–	–	0,22	2,86	0,34	0,11	0,17	0,83	5,65	0,81	29,07	43,32	42,34	28,50	36,26	48,01	46,94
Ti	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,03	0,03	0,03	–	–	–	0,01	0,02	–	–
OH	0,78	0,34	3,22	20,46	1,00	2,66	2,36	3,66	8,58	23,72	24,22	8,40	9,04	22,94	17,58	11,10	9,52
Fe^{2+}/Fe^{3+}	10,85	7,78	0,90	0,90	5,06	1,52	4,77	6,23	8,11	0,18	0,15	0,00	0,04	0,00	0,05	0,13	0,00
N_9/K	6,50	9,33	9,17	5,50	5,09	7,8	6,64	12,00	2,45	6,40	4,00	2,00	3,00	5,00	4,50	3,80	2,25
OH+C	0,78	0,34	3,44	23,32	0,51	2,77	2,53	4,49	14,23	24,53	53,29	51,72	51,38	51,44	53,84	59,11	56,46
Ca + Mg	40,13	34,95	44,91	45,45	41,41	39,02	36,68	29,67	39,21	35,96	42,98	45,22	45,15	38,66	47,50	43,55	43,71

trace amounts. The use of OH and C + OH is therefore considered unsatisfactory.

The ratio Fe^{2+} / Fe^{3+} was rejected as unsuitable on the grounds that iron is present in a number of different primary minerals (olivine, augite, bronzite and magnetite), which occur in varying proportions and which weather at different rates.

In addition, the clearest trends are obtained when the numbers of ions in the standard cells are plotted against the number of C ions : more complex relations are suggested by the use of OH, C + OH and Fe^{2+} / Fe^{3+} as reference standards.

4.3.4. Behaviour of the elements

The behaviour of the various elements was analysed separately for the peridotites and pyroxenites because of the differences in composition of the two rock types. The position of the strongly altered rocks is again problematical; the variations displayed by these rocks show approximately the same degree of misfit when plotted with the peridotites or the pyroxenites, except for Fe^{2+}, Fe^{3+} and OH. In the case of the latter three elements the strongly altered rocks are quite incompatible with the pyroxenites and for this reason were classified with the peridotites. In order to illustrate the differences displayed by the three different rock types the strongly altered rocks and peridotites are distinguished in Figures 6, 7 and 8 and two pyroxenite samples plotted on these diagrams, while one sample of strongly

......./ altered .....

altered rock was plotted on the pyroxenite diagrams (Figures 9 and 10).

4.3.4.1. Peridotites and strongly altered rocks

The variations of Si, Al, Ca, Mg, Na, K, OH, Fe^{2+} and Fe^{3+} as a function of the number of C atoms per standard cell are shown in Figures 6, 7 and 8. The trends are rather erratic, which may be explicable in terms of the difference in composition of the starting materials, although systematic incompatibilities between the peridotites and strongly altered host rocks are obvious.

Si shows a marked decrease with increasing alteration, while Al also decreases, but at a slower rate (See Figure 6A).

Ca and Mg display a strongly antipathetic variation (Figure 6B). If the lines of best fit through all the points for Mg and Ca respectively are drawn the loss of a small amount of Mg and the gain of a little Ca is suggested. Total Ca + Mg remains approximately constant.

Figure 7A indicates an increase in OH during the early and middle stages of alteration, followed by dehydration.

Fe^{2+} and Fe^{3+} both decrease with increasing C content and the ratio Fe^{2+} to Fe^{3+} also decreases (Figures 7B and 7C).

.........../ Na .....

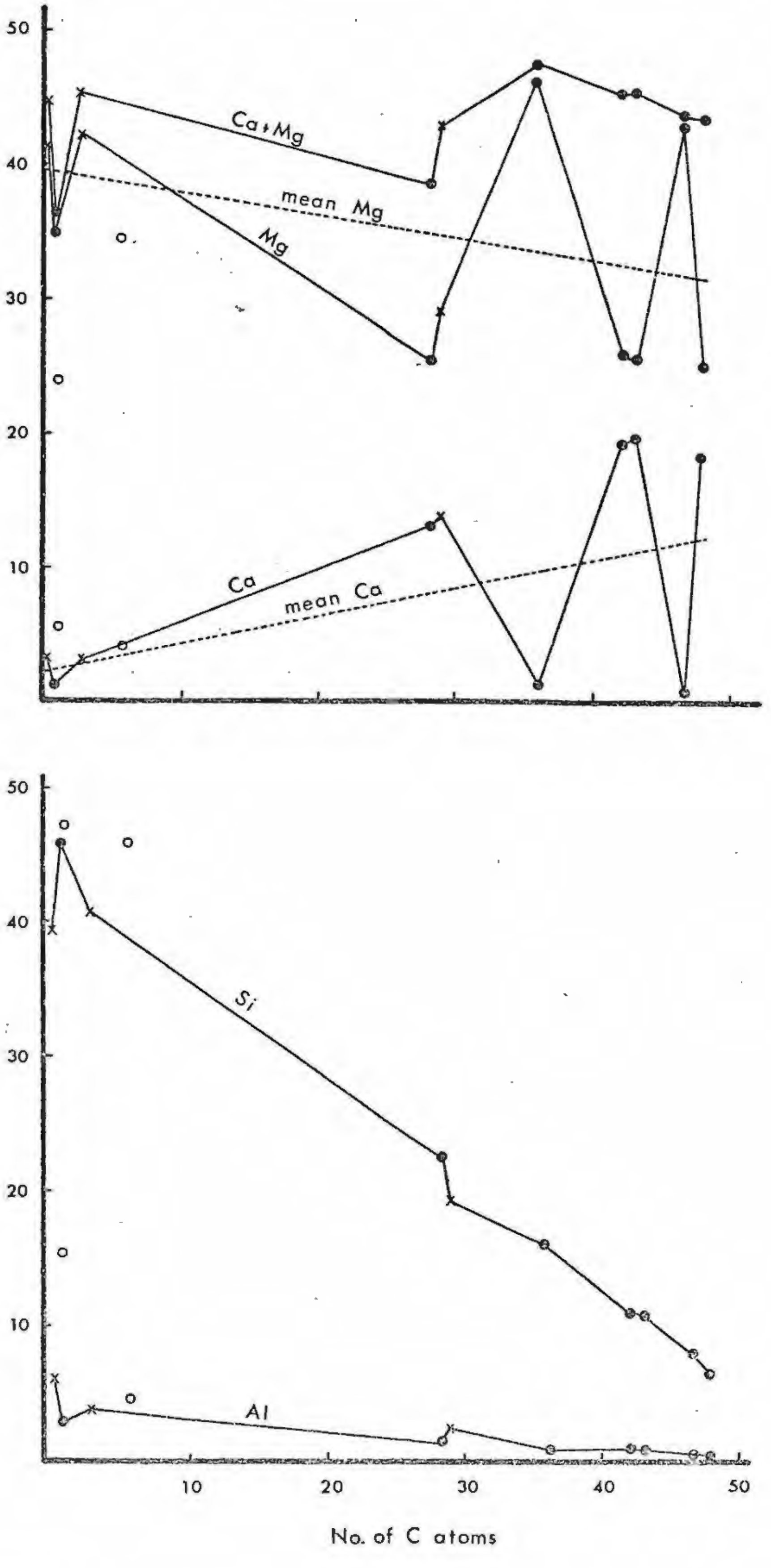


FIGURE 6 :

Chemical variations displayed by the peridotites (crosses) and strongly altered parent rocks (black circles); two pyroxenite samples (open circles) are shown for comparison. The numbers of the ions per standard cell are plotted against the corresponding number of C atoms.

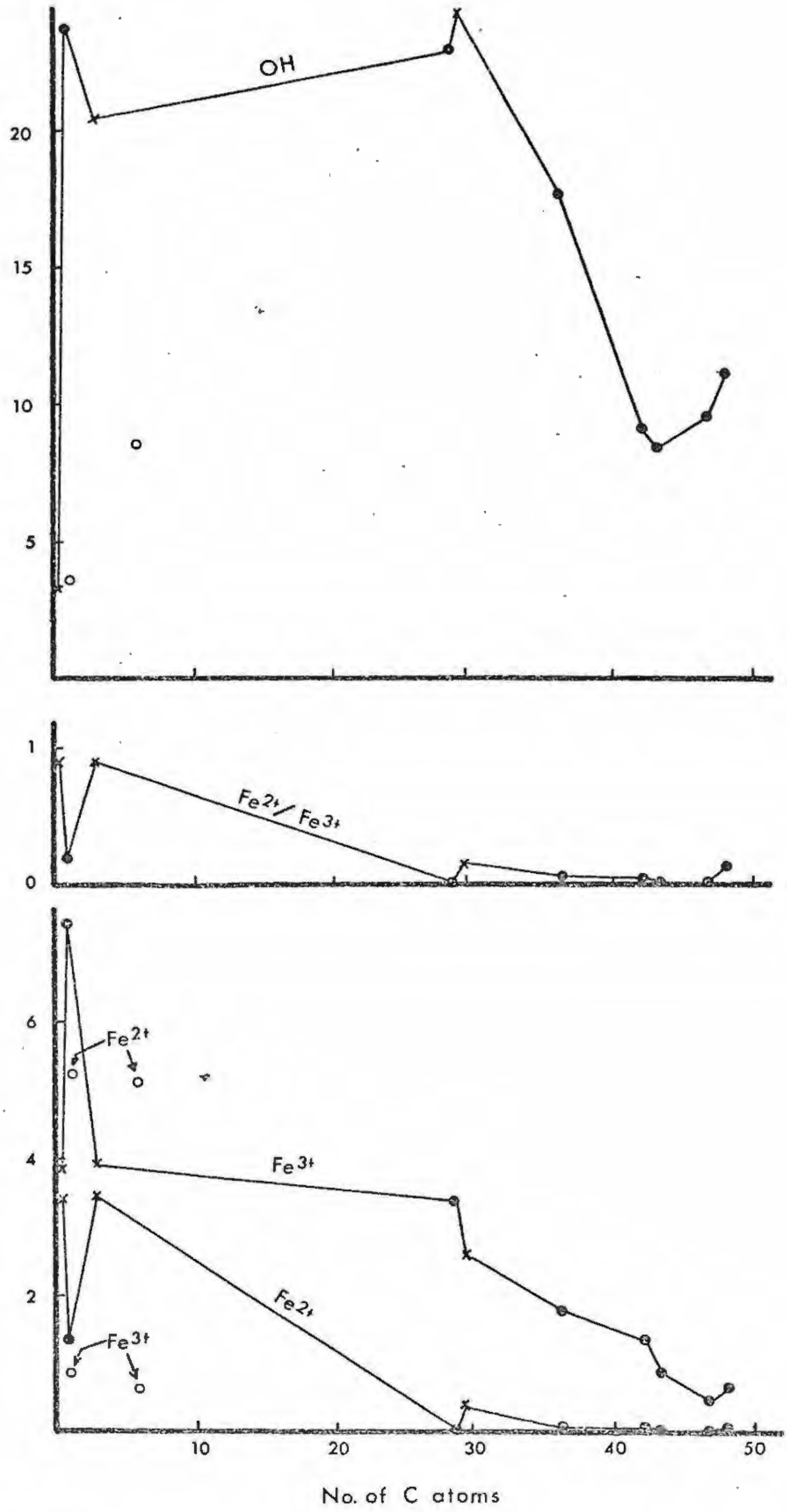


FIGURE 7 :

Chemical variations displayed by the peridotites (crosses) and strongly altered parent rocks (black circles); two pyroxenite samples (open circles) are shown for comparison. The numbers of the ions per standard cell are plotted against the corresponding number of C atoms.

Na displays a distinct decrease, while K remains constant (Figure 8A) and consequently the ratio Na/K decreases (Figure 8B).

4.3.4.2. Pyroxenites

Except for OH, which increases with increasing C, none of the elements displays any definite trends (Figures 9 and 10). Si decreases slightly, while Ca and Mg display an antipathetic and Ca and Al a sympathetic relationship.

4.4. Conclusion

It should be stressed that the method used above to interpret the chemical relationships displayed by the altered rocks is based on the principle of isovolumetric change. No positive evidence for this was found, although it seems a reasonable assumption in the light of previous studies.

The relative compatibility of the chemical trends shown by the strongly altered host rocks with those of the peridotites and their incompatibility with the variations displayed by the pyroxenites gives support to the tentative conclusion drawn in Section 3.6. regarding the original nature of the strongly altered rocks i.e. that they are strongly altered peridotites. This evidence, however, is by no means conclusive.

If the strongly altered rocks do in fact represent original peridotites, then the alteration of the peridotites is effected by carbonation, loss of Si and small amounts of Al, Mg and Na, a

........../ small .....

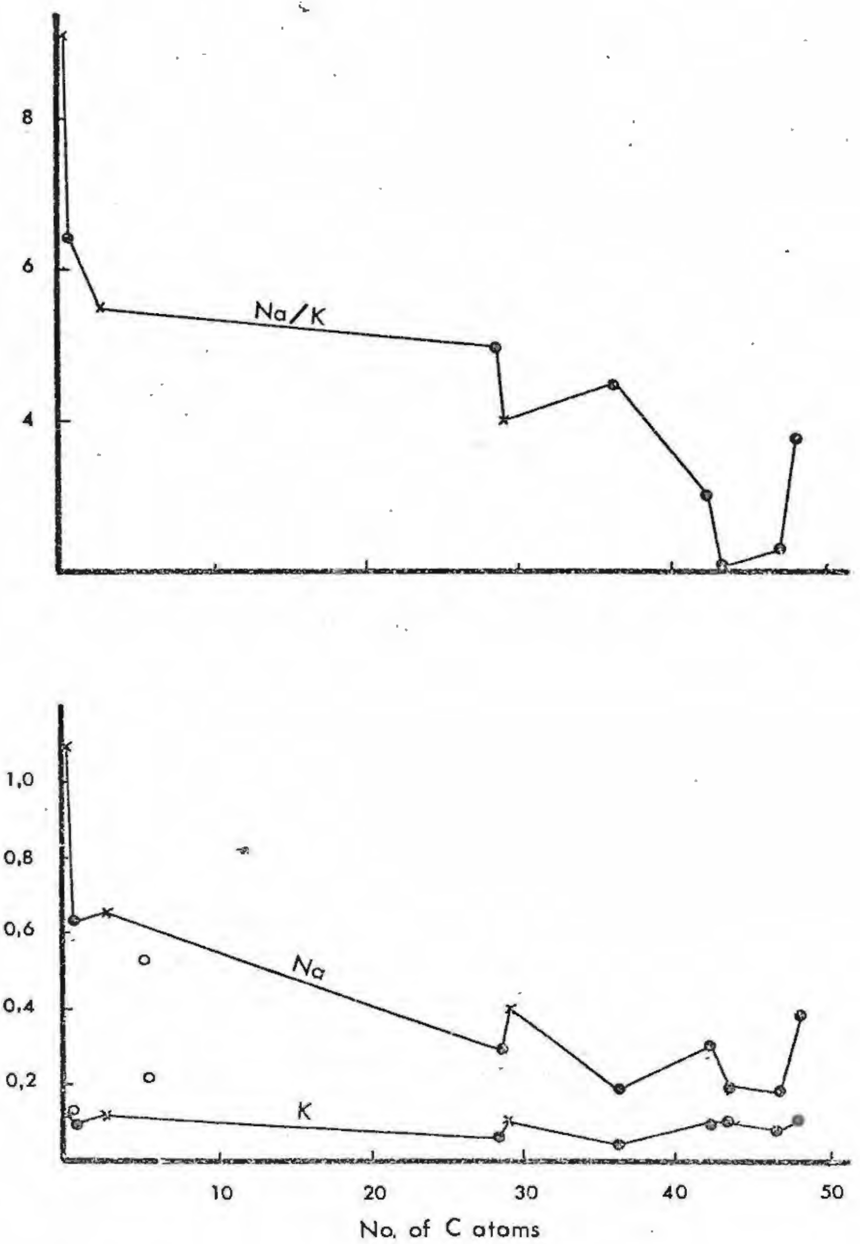


FIGURE 8 :

Chemical variations displayed by the peridotites (crosses) and strongly altered parent rocks (black circles); two pyroxenite samples (open circles) are shown for comparison. The numbers of the ions per standard cell are plotted against the corresponding number of C atoms.

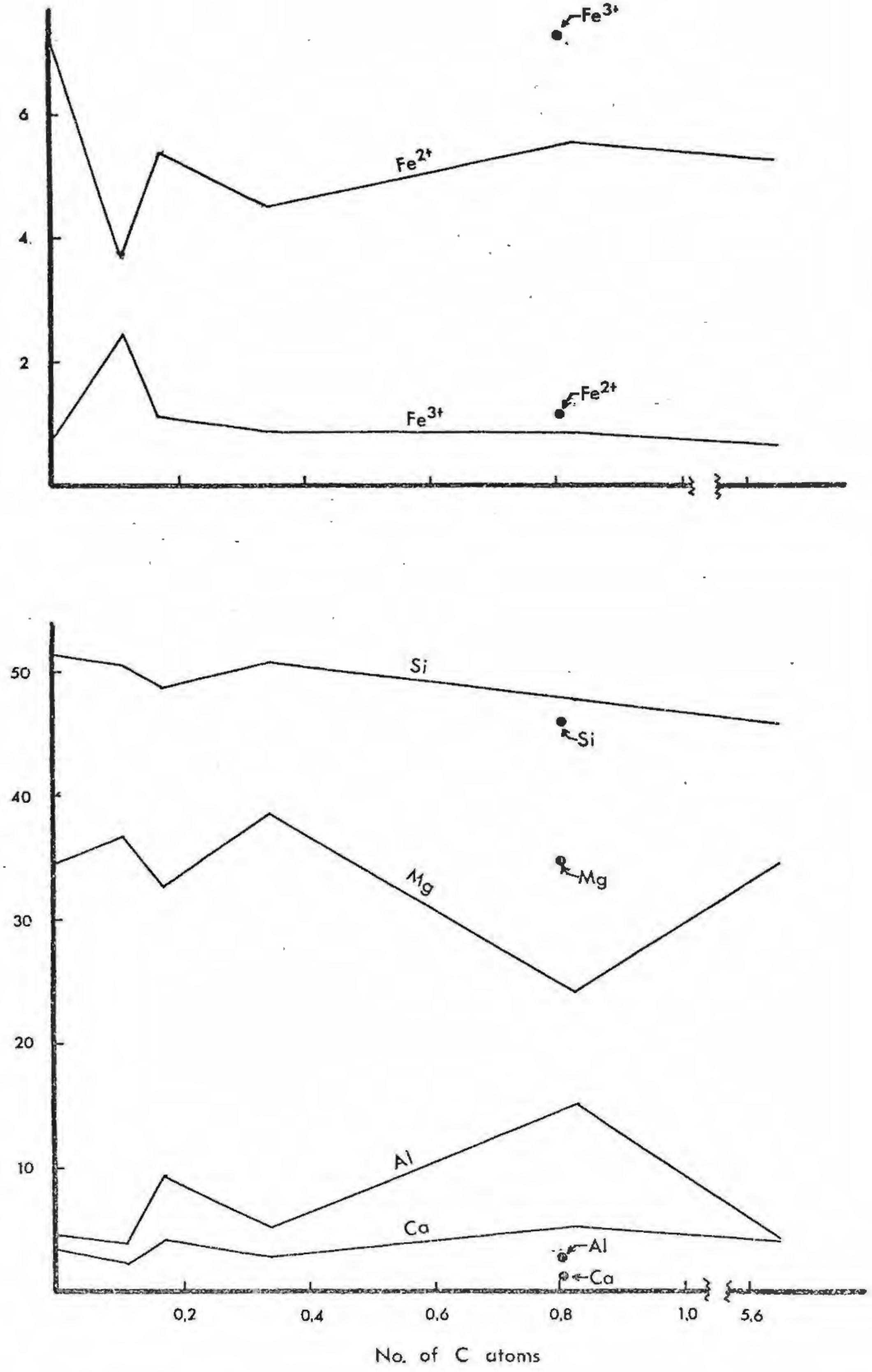


FIGURE 9 :

Chemical variations displayed by the pyroxenites with one sample of strongly altered host rock shown for comparison.

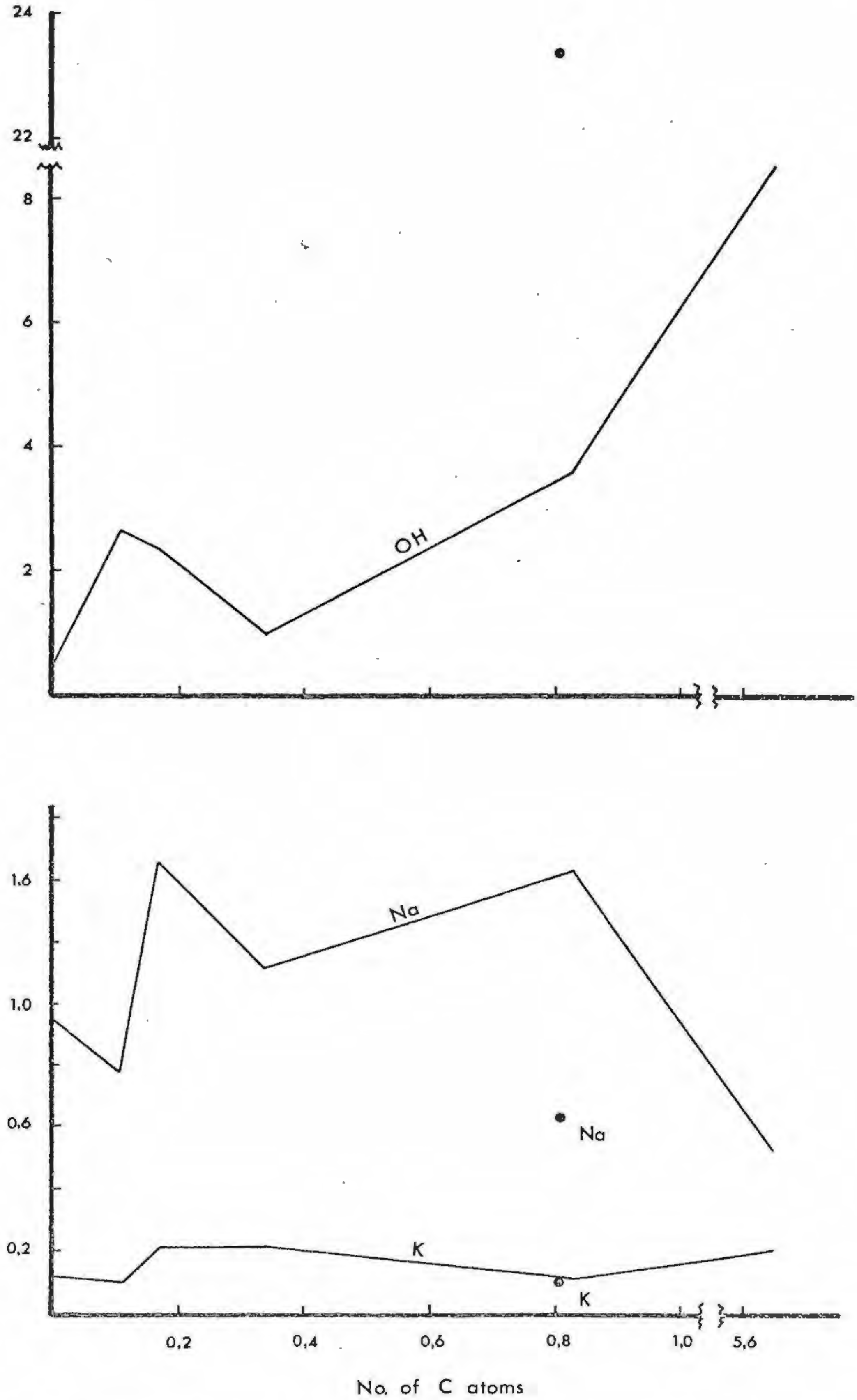


FIGURE 10 :

Chemical variations displayed by the pyroxenites with one sample of strongly altered host rock shown for comparison.

small increase in Ca, the early oxidation of the iron and removal of both Fe^{2+} and Fe^{3+}, hydration during the early and middle stages followed by dehydration.

The analyzed pyroxenite samples represent only the early stages of pyroxenite alteration : the most strongly altered sample (P9) contains only 5,65 C atoms per standard cell, compared with the corresponding figure of 48,01 for the strongly altered host rocks. Alteration of the pyroxenites is initially achieved by carbonation, hydration and the loss of a little Si.

five

genesis

5.1. Field considerations

Since the mineralogical evidence provides no conclusive proof regarding the processes effecting the alteration of the host rock (Environment B), nor the origin of the massive magnesite deposits (Environment A), it is necessary to look to the field characteristics for evidence.

5.1.1. Host rocks

It is evident that the magnesite, dolomite and quartz contained in the altered pyroxenite and peridotites represents the familiar quartz-carbonate assemblage derived from ultrabasic rocks, reviewed in Section 1.4.1. Field evidence in support of the alteration of the host rocks by hydrothermal processes is quite insignificant. The granite

........../bodies .....

bodies are very limited in size and show no preferred association with the carbonate-bearing host rocks; on the contrary, granite veins were found in only one carbonate occurrence, where it appears that the carbonate was formed after the intrusion of the granite. Similarly, there is no spatial connection between the dolerite dikes and the carbonate. No hot springs occur in the area.

On the other hand, the structures exhibited by the skeletal, zebra, vein and nodular ore are all explicable in terms of an origin by supergene chemical weathering during which the elements constituting the carbonate minerals undergo at least partial solution and transportation from their sources of derivation. It seems probable that the zebra ore is produced by the alteration of peridotite along shear planes or closely spaced joints and that the skeletal ore represents altered pyroxenite in which the carbonate has become concentrated along regular or irregular openings in the rock. The vein ore, which invariably occurs together with the zebra or skeletal ores is undoubtedly formed by the precipitation and/or deposition of carbonate in fractures or faults. A mode of formation analagous to that of caliche seems most appropriate for the nodular ore, which, in fact, can be described as an unconsolidated highly magnesian caliche.

The occurrence of the carbonate on fairly steep slopes and its absence in drainage channels indicates that it is formed only when the ratio of chemical to mechanical weathering is favourable.

......../ 5.1.2. .....

5.1.2. Massive ore

As in the case of the carbonate-bearing ultrabasic rocks, no evidence for a hydrothermal mode of origin could be found for the massive magnesite, while the shallow vertical persistence of the ore points convincingly to an origin by supergene processes. The massive ore may therefore represent the product of one or more of three processes :

(a) In situ weathering of a favourable stratigraphic horizon.

(b) In situ weathering of material transported from elsewhere.

(c) Precipitation and/or deposition in a favourable trap of magnesite formed elsewhere and transported to the present sites.

(a) is inconsistent with the independence of the ore of structural control. The persistence of relatively unaltered rounded boulders and pebbles of pyroxenite down to a depth of at least 8m argues against both (a) and (b). The explanation given by VAN ZYL et al. (1942) thus seems the most feasible :

> "Transpiration of magnesite-bearing ground waters through porous soil and subsoil has resulted in the accumulation of magnesite nodules and lumps in some localities."

Such a mode of formation is in accordance with the

......./ shallow

VAN ZYL et al. 1942, p.45

shallow vertical persistence of the massive ore, its occurrence only on flat-lying or gently sloping ground below the hill slopes, and with its absence in drainage channels, where the surface and subsurface waters are more mobile, inhibiting the precipitation and/or deposition of appreciable quantities of carbonate.

That the clean magnesite nodules found on the surface crystallised from a gel is suggested by the presence of colloform banding (Plate 7B), septarian cracks (Plates 7C and 7D) and botryoidal habit (Plate 7D), although the traditional view regarding the origin of colloform textures has been challenged by ROEDDER (1968) who argues that most of the textural criteria proposed for recognising colloidal deposition is ambiguous and that most colloform textures are explicable in terms of a relatively high supersaturation and hence relatively high nucleation and growth rate.

5.1.3. Relationship between Environments A and B

The striking physiographic relationship between the carbonate derived from the weathering of ultrabasic rocks situated on steep slopes (Environment B) and the shallow blanket-like deposits situated down-slope on flatter ground (Environment A) points to a genetic connection between the two. In the light of the explanations advanced in Sections 5.1.1. and 5.1.2. above concerning the modes of formation of the carbonate occurring in the two distinct environments, it seems obvious that the material derived from the chemical breakdown of the ultrabasic rocks in a zone of active

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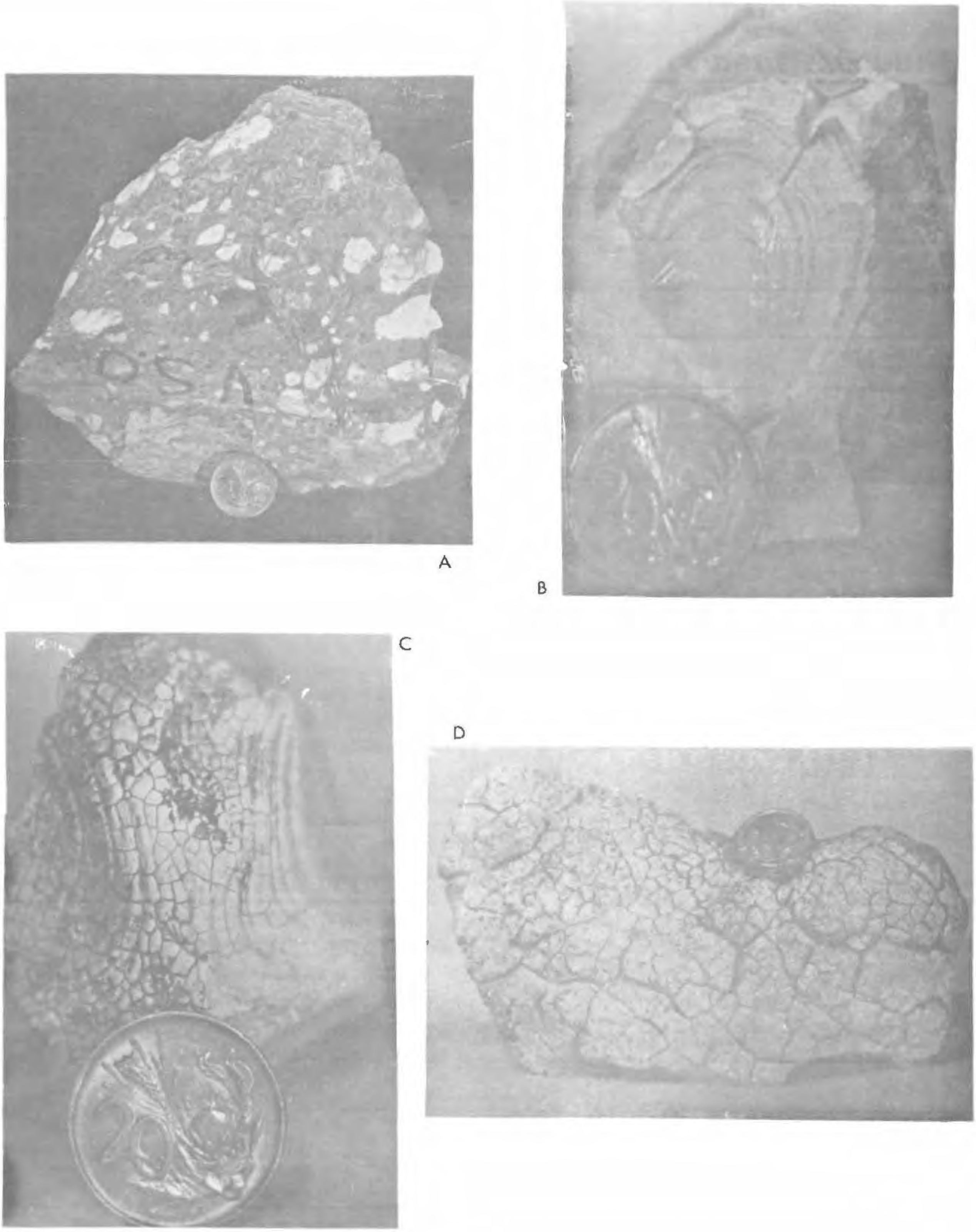

PLATE 7.

A. Typical blanket reef in which irregular magnesite nodules are set in a ferruginous calcrete matrix.
B. and C. Surface nodule of magnesite displaying colloform banding (B) and septarian cracks (C).
D. Surface nodule with botryoidal habit and septarian cracks filled with ferruginous calcrete.

chemical weathering (Environment B) is transported in solution and/or suspension and precipitated and/or deposited under favourable physico-chemical conditions (Environment A). Two aspects, therefore, warrant closer investigation :

(a) The milieu in which the parent peridotites and pyroxenites are chemically weathered.

(b) The physico-chemical conditions responsible for the transportation of the products of weathering and the deposition of some or all of these during the formation of the massive ore.

5.2. The weathering of basic and ultrabasic rocks

Ideally this part of the thesis would have employed thermochemical reasoning to explain the progressive weathering of the parent rocks and the precipitation of the secondary minerals. Unfortunately, the science has yet to reach the stage where such an approach would be possible : thermodynamic data on the weathering of rocks and minerals are virtually non-existent, while the stability relations of many minerals - particularly the carbonates - still provide a subject for much debate. In addition, no analyses were made of either the initial weathering solutions or the waters which have washed over the rocks and which could be collected in the drainage channels immediately after a rainstorm. The discussion that follows is, therefore, no more than a qualitative survey.

5.2.1. General remarks

Chemical weathering is a process whereby the component minerals of a rock in contact with an aqueous

........../ solution ......

solution are incongruently dissolved and new phases precipitated from the solution (GARRELS, 1959; LOUGHNAN, 1969; CARROL, 1970; FRIPIAT and HERBILLON, 1971; HELGESON, 1972).

The ultimate source of the solutions responsible for weathering is rainwater.BAAS BECKING et al. (1960) have measured the oxidation potential and acidity of rainwater and found the Eh values to centre around 400-700 and the pH around 4 - 6. CARROL (1970) describes rainwater as a mixed electrolyte containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^- and SO_4^{2-} as the major constituents, with lesser quantities of ammonia and other nitrogen compounds, iodine, bromine, boron, iron, aluminium and silica.

Solution of the rocks through which the rainwater percolates radically alters its composition. BARNES and O'NEIL (1969) have found that the surface and shallow ground waters discharged from serpentinites are rich in $Mg^{2+}$and HCO_3^- and have alkaline pH values; their observations are supported by WHITE et al. (1963) (See Table XII) and by LESKO (1972) (See Section 1.4.5.3.).

The breakdown of the parent minerals is effected by hydrolysis - the replacement of cations in the mineral structure by H^+ ions from the solution. Silicate hydrolysis involves three separate steps : (a) reaction of the mineral with an aqueous solution with which it is out of equilibrium, (b) reactions among species in the aqueous phase, and (c) reactions between the aqueous solution and stable and/or metastable phases precipitated from solution (HELGESON, 1972). HELGESON (op.cit.) has demonstrated that the rate determining

.........../ step .....

step in this process is the diffusion of material out from the reactant mineral. H^+ ions are derived mainly from the dissociation of the water molecules, a process which is promoted in part by unsatisfied charges on the mineral surfaces (FRIPIAT and HERBILLON, 1971). Carbonic acid is formed by the solution of CO_2 from the atmosphere or from the air in soil pores, which is often strongly enriched in CO_2 (WHITE et al. 1963). Although H_2CO_3 is a weak acid and the degree of dissociation slight, the analyses listed in Table XII show that large quantities are present in ground waters. LOUGHNAN (1969) has postulated that the pH of ground waters may also be lowered by the exchange of cations with H^+ ions from root hairs.

Replacement of cations in the crystal lattice by H^+ ions results in a large charge-to-radius ratio and a rupturing of the chemical bonds (LOUGHNAN op.cit.). Incongruent solution occurs when two or more different minerals are in contact with the same solution. The persistence of certain minerals in solutions with which they are not in equilibrium may be explained in terms of slow reaction rates or an armouring effect : for example, feldspar is frequently protected by a coating of H-feldspar and magnetite by a thin layer of hematite (GARRELS, 1959).

The ease with which minerals are weathered depends primarily on the crystal structure and secondarily on the nature of the cations within the lattice (LOUGHNAN, op.cit., LING ONG, 1971). The nesosilicates, in which isolated SiO_4 tetrahedra are held together by cations, are most easily disrupted by replacement of the cations. The three-dimensional Si-O linkage in the tectosilicates, on the other

........../ hand .....

TABLE XII.

Chemical analyses of ground waters from ultramafic rock types.

	1(ppm)	2(ppm)	3mg/ℓ)	4(mg/ℓ)
SiO_2	50	16	31	22
Ca^{2+}	9,6	2,5	7,9	14
Mg^{2+}	35	7,7	260	72
Fe^{2+}		0,08	-	
Na^+	5,8	0,2	10	5,5
K^+		0	0,3	0,7
HCO_3^-	168	44	1353	434,2
CO_3^{2-}	0	0	109,2	4,05
Cl^-	14	0,7	34	12
SO_4^-	0,5	0	13	5,4
T°C			30	26,7
pH	7,6	8,5	8,97	8,15

1 : Bushveld ultramafics, Pretoria District (WHITE et al. 1963).
2 : Peridotite, Webster, U.S.A. (WHITE et al. op cit.)
3 : Serpentinite, Moutery, California (BARNES and O'NEIL, 1969).
4 : Partially serpentinised peridotites and dunites, Mountery, California (BARNES and O'NEIL, op cit.).

hand, results in minerals of this group being relatively resistant to weathering. The tectosilicates are more resistant than the sheet silicates, whose basic structure consists of a two-dimensional Si-O framework, and these in turn are less easily weathered than the chain silicates in which Si-O links occur in one direction only.

Al-O bonds are weaker than Si-O bonds due to the difference in electronegativities of Al and Si and the greater polarization of the electrons comprising the Al-O link. Consequently the calcic feldspars are more susceptible to weathering than the alkali feldspars. The same principle holds for the cations associated with the silicate lattice. For example, forsterite is more easily weathered than fayalite because of the greater ionic character of the cation-silicate bond in the former as a result of the greater electronegativity of the Mg^{2+} ion.

Although the initial composition of the weathering solutions is acidic, the pH rapidly increases as alkali and alkaline earth ions are dissolved out of the rock and H^+ ions removed from solution (CARROL, 1970; LOUGHNAN, 1969). Removal of the cations is accompanied by the solution of silica and alumina at a much slower rate : over the pH range characteristic of the weathering environment alumina is less soluble than silica, resulting in residual enrichment of the former and the formation of alumina-rich clays (CARROL op.cit.).

The replacement of metallic cations by H^+ ions and the attendant breakdown of the mineral structures rapidly reaches equilibrium unless some of the constituents are leached from the environment. Climate and topography

........../play ......

play the major roles in influencing the rate of chemical weathering by retarding or accelerating the leaching process (LOUGHNAN op.cit.). Aapiesboomen is characterised by a semi-arid climate in which long, hot, dry spells separate the rains, which occur mainly in the form of short thunder storms. Under such conditions some of the soluble material would be removed during and immediately after the rains when large volumes of water are produced in a short time. During the dry periods, however, much or all of the water which penetrated the rocks would be lost by evaporation resulting in high pH values, the slowing down of the weathering process and the precipitation of carbonates. Such conditions would also favour oxidation and a general paucity of organic matter.

Of the common rock-forming cations Ca^{2+}, Mg^{2+} and Na^{+} are readily lost under leaching conditions; K^{+} behaves similarly, although it may become fixed in some crystalline phase such as illite (CARROL op.cit.). The fate of iron depends on both the rate of leaching and the redox potential. The Eh increases with increasing pH and iron is therefore more readily oxidized in an alkaline medium (LOUGHNAN op.cit.). Fe^{2+} is very susceptible to oxidation and Fe^{3+} is virtually immobile unless complexed with certain inorganic or organic ions or with natural chelating agents (WHITE et al. 1960, SCHALSCHA et al. 1967).

The solubility of quartz at 25°C appears to be around 6 p.p.m. and that of amorphous silica between 100 and 140 p.p.m. The solubilities of silica from the common silicate minerals is unknown (KRAUSKOPF, 1959; SIEVER, 1957, 1962). KRAUSKOPF (op.cit.) considers most silica in

............/natural .....

natural waters to exist in true solution as monomeric silicic acid. Experimental work shows that at constant temperature solubility is independent of pH at pH values below 9; ionization of the H_4SiO_4 above this figure increases the solubility abruptly. SIEVER (1957) suggests that in dilute solutions H_4SiO_4 is probably hydrated, with one layer of water molecules surrounding the $Si(OH)_4$ tetrahedra, and at pH values exceeding 9 other species such as silicate ions and polymeric forms of silicic acid appear as a result of the ionization of the monomeric molecule. In the view of FRIPIAT and HERBILLON (1971) the silica liberated during weathering forms polymeric hydrated SiO_2, the degree of polymerization being pH dependent. In general, the degree of polymerization appears to be higher at higher pH, although maximum polymerization seems to occur at pH values of between 4 and 4,5. These authors have found the solubility of silica to be affected by the presence of cations, especially Mg^{2+} and Al^{3+}, which cause the precipitation of silico-alumina and silico-magnesia amorphous and crystalline phases.

The behaviour of alumina during weathering is complex and depends on the pH, temperature and the nature and concentration of other soluble constituents. In addition, aluminium hydroxide tends to form colloidal or subcolloidal suspensions (HEM and ROBERSON, 1967). In general, alumina is practically insoluble over the pH range between 4 and 8,5. In acid solutions (pH 2,85 - 4,07) alumina exists as $Al\ (OH)_2^{+}$ and in alkaline solutions (pH10-12,5) as $Al\ (OH)_4^{-}$ with an isoelectric point at pH 6,70; under strongly acid conditions the species Al^{3+} is stable (REESMAN et al. 1969). FRIPIAT and HERBILLON (1971), on the other hand, consider the

........../ aluminium .....

aluminium liberated during hydrolysis to be present in the weathering solutions in the form of polynuclear complexes and that the coordination number of Al in the new solid phase depends on the pH of the environment. Under alkaline conditions the tetrahedral coordination is favoured in which Al is connected to O and carries a negative charge, while in acid medium Al tends to crystallize in octahedral coordination, where it is bonded to a variable number of OH groups and carries no charge.

The physico-chemical milieu plays the dominant role in determining the identities and relative rates of precipitation of the secondary minerals formed by weathering processes (FRIPIAT and HERBILLON op.cit. ; HELGESON, 1972). In general the high potential energy barrier of the oxygen lattice prevents solid state diffusion of the cations and transformation processes are more satisfactorily explained in terms of a complete dissolution of the parent species, followed by the neosynthesis of secondary products. Exceptions to this rule, such as the formation of vermiculite from mica, are rare (FRIPIAT and HERBILLON op.cit.).

GARRELS (1959) has shown that, although simple ions and molecular species in solution generally react swiftly and equilibrate in seconds or minutes, polymerized ions may require periods of days or weeks for condensation or disaggregation, and that the formation of silicate and carbonate precipitates is a very slow process. In addition, the first solid to form, although it is in equilibrium with the solution at the time of precipitation, is seldom stable with respect to the other solid phases. Thus, although a change in a natural solution may produce a precipitate simultaneously, a considerable time interval may elapse before true equilibrium is reached.

5.2.2. Peridotites

5.2.2.1. Parent Minerals

(a) Olivine

Microscope studies on the Aapiesboomen peridotites support the theoretical conclusion that olivine is the first mineral phase to be attacked by the weathering solutions. Removal of the Mg^{2+} and Fe^{2+} cations by hydrolysis releases the SiO_4 tetrahedra and, if the rate of release exceeds the rate of solution of the silica the tetrahedra polymerise into sheets, fixing some of the Mg^{2+} and leading to the formation of serpentine (LOUGHNAN, 1969). The iron derived from the olivine may go into magnetite or, if oxidation is particularly rapid, result in limonite formation : it seems that both processes are operating on the Aapiesboomen peridotites.

(b) Feldspar

Contrary to the predictions of LOUGHNAN (op.cit.), detectable alteration of feldspar occurs before that of the pyroxenes. This occurs through the exchange of Na^+ and later Ca^{2+} ions for H^+ from the solution and the enrichment of Si and Al (LOUGHNAN, op.cit.; CARROL, 1970;

............/ HELGESON ......

HELGESON, 1972). The formation of an outer layer of H- silicate and the consequent retardation of the alteration (GARRELS, 1959) may be responsible for the persistence of feldspar in some of the strongly altered rocks. With increasing loss of the metallic cations, the $(Si, Al)O_4$ tetrahedra tend to polymerise into sheets resulting in the formation of montmorillonite, which is itself destroyed and replaced by kaolinite with increasing concentration of Si and Al; leaching of silica finally results in the formation of gibbsite (CARROL, op.cit.). None of these products were detected in the Aapiesboomen rocks.

(c) Pyroxene

Pronounced cleavage parallel to the silicate chains in the pyroxenes provides access to water and facilitates the replacement of the Mg^{2+}, Ca^{2+}, Fe^{2+} and Fe^{3+} cations. This generally leads to polymerisation of the chains into montmorillonite or chlorite or both (LOUGHNAN op.cit.). Again, none of these secondary minerals was detected in the Aapiesboomen peridotites. The ortho- and clinopyroxenes appear to be equally susceptible to alteration.

(d) Oxides

Magnetite is normally oxidized to limonite or hematite and its persistence in the strongly altered rocks and massive magnesite deposits is probably due to a thin coating of oxidized material

GARRELS, 1959).

The chromite is also very resistant to alteration. CERNY (1968) suggests that the persistence of chromite in chrysotile-lizardite serpentinites and its alteration to Cr-chlorite and magnetite in antigoritic serpentinites may be due to pre-serpentinization events : the alteration of chromite appears to be governed by the availability of water and by higher temperatures than those required for serpentinization.

(e) Phlogopite

Information on the secondary formation of phlogopite is scant, although it seems well established that the mineral is altered to vermiculite, which in turn is replaced by chlorite under weathering conditions (BASSETT, 1960; AITKEN, 1965; BESSON et al. 1968).

BESSON et al. (1971) have demonstrated the possibility of the formation of interstratified phlogopite-vermiculite at relatively low temperatures, while SHMAKIN (1964) has shown that the metasomatic formation of phlogopite is achieved by an increase in the chemical potential of K relative to Na and to an introduction of alkalies.

5.2.2.2. Secondary minerals

(a) Serpentine

Two problems present themselves

when considering the formation of chrysotile at the expense of olivine in the Aapiesboomen peridotites :

(i) Whether the process occurred prior to or after the emplacement of the peridotites.

(ii) The particular conditions resulting in the formation of chrysotile rather than one of the other serpentine minerals, lizardite or antigorite.

It is well established by field and microscopic observations and by theoretical considerations that the olivine-rich rocks at the base of the Bushveld Complex were produced by the cumulus sinking of early olivine grains either before or after emplacement, and that, in either case, no serpentine was present at the time of emplacement (WILLEMSE, 1964; WAGER and BROWN, 1968).

PUGIN (1971) notes the existence of two points of view regarding the nature of the differences between the serpentine minerals : one states that lizardite, chrysotile and antigorite are polymorphs of $Mg_3Si_2O_5(OH)_4$, while the other asserts that the structural differences are caused by slight variations in the chemical composition. If the former view is true, then the identity of the mineral formed would depend only on the

........./ temperature .....

temperature and pressure, whereas if the minerals differ in composition the identity of the species formed might be governed by the chemical milieu.

Experimental work by GILLERY (1959) suggests that the chemical composition of the starting materials determines the polytype formed by the crystallization of a gel, fibrous varieties being produced only when the number of Al ions per unit cell is less than 0,24 above which value platy serpentines form. PAGE (1968a) reported finding distinct chemical differences between the three serpentine species, but a detailed analysis of the same data by WHITTAKER and WICKS (1970) casts considerable doubt on these conditions.

Earlier work (for example BOWEN and TUTTLE, 1949; FAUST and FAHEY, 1962) led to the acceptances of a hydrothermal origin for serpentinites. More recent studies, however, reveal the possibility of the process occurring under Earth-surface or near-surface conditions.

BARNES et al. (1967) and BARNES and O'NEIL (1969) have found highly alkaline waters (pH 11,25-12,01) rich in calcium hydroxide derived from partly serpentinized ultramafic rocks in the western U.S.A. These waters are quite distinct from the more usual magnesium bicarbonate meteoric waters generally taken to be the weathering products of ultramafic rocks. The calcium hydroxide waters are unsaturated with respect to Mg-olivine and Mg-pyroxene and

.........../supersaturated ......

supersaturated with brucite and serpentine. The authors conclude that the waters are responsible for the low-temperature surface serpentinization of the rocks and that the process occurs at nearly constant composition, except for the loss of CaO.

Isotope studies by WENNER and TAYLOR (1973) clearly indicate that chrysotile-lizardite serpentinites form at distinctly lower temperatures than the antigoritic equivalents. These findings give support to the view of the authors that meteoric ground waters and/or connote brines may be important in the formation of many continental lizardite-chrysotile serpentine bodies and that deep-seated metamorphic waters seem to be responsible for most continental antigorite serpentinization. The authors suggest a lower limite of 85°C for the formation of lizardite-chrysotile assemblages, but concede that their findings may hold only for the types of Alpine serpentinites covered by the study, which do not include the ultramafic rocks of layered complexes.

Brucite is a common minor constituent of Alpine-type serpentinites, which indicates formation according to the reaction (THAYER, 1966) :

$$\text{olivine} + \text{water} = \text{serpentine} + \text{brucite} + SiO_2.$$

The absence of brucite in some serpentinites has been explained (PAGE, 1968b) as being due to

.........../ either ......

either the reaction between the brucite and CO_2 to form magnesite, or formation according to the reaction :

olivine + enstitite + H_2O + O_2 = chrysotile +
lizardite + magnetite.

The textural, mineralogical and field characteristics of the Aapiesboomen peridotites indicate that serpentinization proceeded under Earth-surface conditions via a reaction analagous to the last one shown above, without the involvement of the pyroxene or the production of detectable lizardite. The concludions are compatible with the view expressed by DE VILLIERS (1970) that the serpentinization of the harzburgite which crops out south of Potgietersrust was controlled by the circulation of ground waters.

WILDMAN et al. (1968) have found that the rate of dissolution of Mg and Si from serpentinites is favoured by increasing CO_2 content of the aqueous solution and that the Mg : Si ratio also increases with increasing CO_2 pressure. The soils associated with serpentinites in California contain much iron-rich montmorillonite, which the authors conclude is formed by concentration of minor Al and Fe in the serpentine relative to Mg to produce the octahedral layer, and the slower dissolution of Si relative to Mg resulting in enough residual amorphous silica in the soil matrix to complete the montmorillonite structure. Thermodynamic evaluation of the stability conditions for brucite, gibbsite and amorphous $Fe(OH)_3$ indicate that the (Fe, Al)-octahedral sheet is more stable than the brucite sheet when in contact with serpentinite soil matrix solutions : the preferential formation of montmorillonite rather than saponite is thus explicable in terms of the greater stability of the dioctahedral sheet (WILDMAN et al. 1971). The authors suggest that the subsequent silication of the octahedral sheet to phyllosilicate layers is achieved by a relatively high concentration of $Si(OH)_4$.

(b) Silica-carbonate

Descriptions of and ideas concerning the processes involved in the alteration of ultramafic rocks to silica-carbonate assemblages have been extensively catalogued elsewhere (See Sections 1.4.1., 1.4.5. and 1.4.6.) and will not be dealt with here. All that need be repeated is that the common anhydrous carbonates are almost certainly preceded by one or more metastable phases, the precipitation of each of which occurs at a particular Mg : Ca ratio of the solution; all require high pH values for precipitation and the dolomite and magnesite precursors crystallize only from strongly saline solutions.

The chemistry of silica crystallization

......./ and ......

and the roles of CO_2 and the carbonate and bicarbonate ions in the transport and precipitation of the alkaline earth metals have not yet been explored and it is appropriate that these subjects be dealt with at this stage.

(i) The roles of CO_2 and the carbonate and bicarbonate ions.

CO_2 is present in pure water, mostly as a dissolved gas (BATHURST, 1971). Some of the CO_2 combines with water to yield carbonic acid :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (1)$$

Dissociation of the acid commences at pH values of about 6 :

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

The reaction :

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (3)$$

proceeds to the right when the pH reaches approximately 7,5, but the bicarbonate ion remains the most abundant anion up to about pH 8,8, whereafter CO_3^{2-} predominates (CLOUD, 1962). These theoretical considerations do not agree with the analyses of ground waters issuing from ultramafic rocks (See Table XII), where the HCO_3^- content far exceeds that of CO_3^{2-}, even where the pH is greater than 8,8. An explanation of this anomaly in terms of the removal of MCO_3 (where M represents a divalent metallic cation) by precipitation is probably not valid, since any such

........./ removal .....

removal would be expected to cause reaction (3) above to produce more CO_3^{2-}. Thus the paucity of CO_3^{2-} relative to HCO_3^- may be due to a metastability as a result of the slowness of reaction (3).

Since equilibrium constants for the reactions :

$$M^{2+} + 2HCO_3^- \rightleftharpoons M(HCO_3)_2 \text{ (aq.)} \qquad (4)$$

$$M^{2+} + CO_3^{2-} \rightleftharpoons MCO_3 \text{ (aq.)} \qquad (5)$$

are not precisely known, it is not possible to predict the solution concentrations at which the soluble complexes are stable. KRAUSKOPF (1967) states that the K values for the association reactions (4) and (5) lie in the range of 10^2 to 10^4 and that the possibility of the formation of soluble carbonate and bicarbonate complexes can be safely neglected in most geologic situations.

However, BATHURST (1971) notes that the activities of both CO_3^{2-} and HCO_3^- are a small fraction of their molalities in sea water, and attributes this to the formation of dissolved ion pairs which prevents all the anions from playing active roles as free ions in the solution. GARRELS et al. (1961) have shown that, in solutions having an ionic strength equivalent to that of sea water, the activity coefficient of CO_3^{2-} is reduced by about 90% and that of HCO_3^- by about 40% on the addition of NaCl and $MgCl_2$ and that the Mg^{2+} ion plays the dominant role in these processes.

........../ one ......

One would expect, therefore, the copious quantities of Mg^{2+} and smaller amounts of Ca^{2+} and Na^+ produced by the weathering of basic and ultrabasic rocks to be present in solutions partly as bicarbonate and to a lesser extent as carbonate complexes and partly as free ions, depending on the ionic strength of the solutions. The degree of complexing increases with increasing solution concentration.

As outlined earlier (Section 5.2.1.) it seems probable that during and immediately after rain the soluble products of weathering at Aapiesboomen are transported down slope, while during the dry periods evaporation of the waters trapped in pore spaces would cause precipitation of the soluble carbonate and bicarbonate complexes by a dual process : loss of CO_2 as a result of increasing temperature and concentration of the soluble constituents by loss of water. A highly simplified representation of the precipitation of the carbonates is given by the reaction :

$$M^{2+} + 2HCO_3^- \rightleftharpoons MCO_3 + H_2CO_3 \qquad (6)$$

The forward reaction is favoured by high pH values, because OH^- reacts preferentially with H_2CO_3 rather than with HCO_3^- (KRAUSKOPF, 1967). Production of H_2CO_3 by reaction (1) would tend to inhibit reaction (6) and therefore the precipitation of carbonates is facilitated by a reduction in the CO_2 pressure.

In the absence of any knowledge concerning

........../ the ......

composition of the pore fluids, it is not possible to give any precise explanation for the early crystallization of calcite and the predominance of dolomite over magnesite during the early stages of carbonate formation. All that can be stated with certainty is that the production of calcite and dolomite must have been governed by relatively high ratios of Ca : Mg in the solutions. Chemical studies of caliche deposits by ARISTARAIN (1970) and GOUDIE (1972) (Section 5.3.3.) indicate that Mg is more soluble than Ca under the conditions responsible for the weathering of the Aapiesboomen rocks and the enrichment of the pore solutions in Ca relative to Mg is therefore probably due to the differential leaching of the latter.

(ii) Silica precipitation

The precipitation of silica in natural solutions is little understood (KRAUSKOPF, 1959). In the laboratory the formation of a colloidal suspension prior to precipitation is commonly observed. In concentrated solutions the colloid may set to a gel or precipitate as flocculent masses, but in dilute solutions the dispersed sol is very stable. Colloidal silica may be precipitated by evaporation, cooling or by the addition of electrolytes. In nature it appears that precipitated silica forms directly a more solid, practically anhydrous material, examples of which are furnished by the opal of spring deposits and chert replacement in sediments. Much evidence also exists to suggest that with time

............/ opal ......

opal crystallizes to chalcedony and the latter to quarts.

(c) Hornblende

The marginal alteration of pyroxene to a pale green amphibole, usually considered to be actinolitic in composition, is a phenomenon commonly observed in basic rocks (DEER et al. 1962b). Secondary hornblende is also not uncommon. Such amphiboles, known as uralites, are generally considered to be the result of the pneumatolytic action of water-enriched late magmatic fluids on the earlier crystallized pyroxenes. Uralite may also be produced by low-grade dynamic, thermal, regional or metasomatic metamorphism, although in many rocks the process cannot be correlated with any specific metamorphic factor.

In a chemical study of the formation of secondary actinolite at the expense of bronzite and endiopside in southern New Caledonia RODGERS (1973) concludes that the amphibole formed under conditions of low-grade dynamic metamorphism, possibly accompanid in places by metasomatism, but that in some localities uralitization continued after the cessation of metamorphism. The author suggests that the process may be effected by the conversion of pyroxene to the amphibole anhydride by means of rotating alternate silica tetrahedra, thus changing Si_4O_{12} groups to Si_4O_{11}, accompanied by the expulsion of excess Ca

........../ and ......

and followed by hydrolysation.

Due to the extremely fine-grained nature of the hornblendes identified in the Aapiesboomen rocks and the absence of experimental data on the crystallization of secondary amphiboles, it is not possible to postulate a satisfactory explanation for the occurrence of hornblende in the strongly altered host rocks. Examination under the microscope did not reveal any preferred concentration of the clay-sized material around pyroxene grains, however, and therefore it seems more likely that the hornblende crystallized from solution rather than by the solid state transformation of pyroxene.

WILSON and FARMER (1970) have observed the formation of an interstratified chlorite-saponite at the expense of a minor iron-rich phase in hornblende under weathering conditions at Rehiran, Scotland,whereas the major Mg-rich phase remains relatively unaltered. In a brief review of the weathering of hornblende, the authors note that the amphibole may be replaced by chlorite, hydrochlorite, chlorite interstratified with vermiculite or some other swelling mineral, or by iron-rich montmorillonite.

(d) Brugnatellite

Brugnatellite is a rare mineral found in minor quantities in veins and crusts in serpentinites (BEDOGNE and PAGANO, 1972). ARTINI (1922) described brugnatellite as an alteration product of brucite veins in serpentinite in Italy. Chemical analyses

........../ show ......

show the mineral formula to be $MgCO_3.5Mg(OH)_3.4H_2O$.

5.2.2.3. Conclusion

The mineralogical changes displayed by the peridotites and strongly altered parent rocks are consistent with the chemical variations exhibited by the rocks, which in turn may be correlated with the theoretical predictions outlined in Section 5.2.1.

The loss of Si and Al (Figure 6A) and of Fe^{3+} (Figure 7B) during weathering point to abnormal conditions, since all three elements are practically insoluble in the 'normal' weathering environment. It seems likely that their mobilities are governed by the moderate to strongly alkaline conditions resulting from the large quantities of alkali and alkaline earth ions, particularly Mg^{2+}, present in the weathering solutions. In the case of Fe^{3+} it is possible that the formation of chelates and other soluble complexes assist in the removal of this element. Similarly, the absence of the 'normal' weathering products of pyroxene (montmorillonite and chlorite), feldspar (montmorillonite, kaolinite and gibbsite), serpentine (montmorillonite), hornblende (chiefly chlorite)and phlogopite (vermiculite and chlorite) may also be related to the unusual chemical environment and/or the semi-arid to arid climate.

Na^+ (Figure 8A) and Mg^{2+} (Figure 6B) would be removed during the periods in which leaching conditions prevail, i.e. during and immediately after

........./ the ......

the rains, while the immobility of K^+ (Figure 8A) is probably due to the resistance of phlogopite to weathering.

The relative enrichment of the rocks in Ca (Figure 6B) with increasing weathering is probably due to the relative insolubility of Ca and/or to the slow breakdown of the feldspar, the most important Ca-bearing mineral : if the latter explanation is correct then it is necessary to postulate that Na^+ is removed from the feldspar at a faster rate than Ca^{2+}. It is possible that the accumulation of Ca is also due in part to the relatively slow weathering of clinopyroxene.

The position of sample P10 in Figures 6, 7 and 8 gives support to the conclusions arrived at in Section 3.6.1., i.e. that P10 represents an early stage in the weathering sequence and that hornblende commences crystallization contemporaneously with or soon after production of the first carbonate. Furthermore, the behaviour of OH (Figure 7A) shows that the formation of hornblende is overshadowed, either relatively or absolutely, by the crystallization of carbonates during the latter stages.

Depletion of the Fe^{2+} content (Figure 7B) indicates that oxidizing conditions prevail throughout the weathering sequence.

5.2.3. Pyroxenites

5.2.3.1. Parent Minerals

No additional features are exhibited

by the pyroxenes and feldspar contained in the pyroxenites.

5.2.3.2. Secondary Minerals

The secondary minerals which crystallize in the weathered pyroxenites are the same as those identified in the peridotites and strongly altered parent rocks, except for hornblende which is absent in the former. As pointed out earlier, however, (Section 4.4., Table XI) the pyroxenites analyzed in the present study represent only the early stages in the weathering sequence and it is possible that detectable quantities of hornblende may be formed at a later stage.

5.2.3.3. Conclusion

The chemical variations displayed by the altered pyroxenites are qualitatively similar to those exhibited during the early stages of the weathering of the peridotites and strongly altered host rocks.

5.3. Formation of the Massive Ore

5.3.1. Silica-carbonate precipitation

As outlined in Section 5.1.3. it seems likely that the Mg^{2+} ions and lesser quantities of Ca^{2+} and silica derived from the weathering of the peridotites and pyroxenites on the hill slopes are precipitated on the flatter ground : this is probably brought about by the penetration of the soil by the solutions as a result of a decrease in velocity, followed by evaporation. The chemistry of the transportation and precipitation of Mg, Ca and Si have been described in Section 5.2.2.2.(b).

5.3.2. Palygorskite

Apart from a few isolated hydrothermal occurrences (e.g. STEPHEN, 1954; BAILEY and TYLER, 1960; BONATTI and JOENSUU, 1968, 1969; SABATIER, 1969), minerals of the palygorskite-sepiolite group are virtually restricted to playa lake environments and arid soils and are unknown in older sediments (LOUGHNAN, 1969). These clays require alkaline, non-leaching conditions for survival and are generally associated with salts and carbonates (GRIMM, 1953; CARROL, 1970a).

Authigenic palygorskite is commonly found associated with dolomite in lacustrine deposits, the constituents of which are derived from the weathering of basic rocks. ROGERS et al. (1954) were the first to describe the occurrence of palygorskite in the Redbank Plains Formation, near Ipswich, Australia. The clay occurs as horizontal and vertical bands 10 - 40 cm thick in dolomite, and in places contains hard brownish cores composed mainly of sepiolite. The authors consider the palygorskite to have been formed by the replacement of sepiolite - derived from the weathering of neighbouring basalts - by the partial isomorphous replacement of Mg by Al in a lacustrine environment. This view is disputed by

.........../LOUGHNAN ....

LOUGHNAN (1960), who considers the sediments to have been laid down in playa lakes, and the main species formed to have been controlled by the Mg-content of the waters. Increasing Mg-content as a result of evaporation resulted in the transformation of first-formed montmorillonite to palygorskite, the latter to sepiolite and finally dolomite was the only phase precipitated. These conslusions are consistent with those reached by HEYSTEK and SCHMIDT (1953) regarding the occurrence of palygorskite associated with montmorillonite and dolomite at Springbok Flats in the Transvaal. The authors consider the palygorskite to have been derived, via montmorillonite, by the progressive weathering of Stormberg basalts.

TIEN (1973) has described palygorskite associated with minor dolomite and calcite in joints in dioritic rocks at Warren Quarry, Enderby, in Leicestershire. The clay is apparently precipitated from solutions rich in Si and Mg derived from the diorites and overlying sediments. A similar occurrence in Switzerland has been ascribed (VERNET, 1967) to precipitation from high-pH interstitial waters rich in silica and alkali and alkaline earth ions.

In a comparison of palygorskite occurrences in the south-eastern U.S.A. and the Yucation Platform, Isphording (quoted by HOWER, 1973) concluded that in both cases the clays, which are associated with limestone, dolomite and chert, were formed by direct crystallization in hyper-saline lagoons adjacent to areas undergoing rigorous tropical and sub-tropical weathering. A Mg- and Si-rich environment is indicated by the presence of dolomite, chlorite, sepiolite and chert.

BERZILIN and MIKHAYLOVICH (1967) have noted intense diagenetic palygorskitization and montmorillonitization of kaolinite and, to a lesser extent, hydromica, in the Cretaceous sediments of the hot, arid Fergana basin in Russia. Palygorskite associated with montmorillonite, calcite, illite and kaolin has also been observed in calcic valley soils derived from the weathering of marls in Israel (RAVIKOVITCH et al. 1960).

In a study of the genesis of sepiolite at Earth-surface conditions, WOLLAST et al. (1968) concluded that the mineral is precipitated from solutions derived from the weathering of ultra-basic rocks only in the absence of aqueous aluminium species and of reactive aluminous solid phases.

To sum up, then, the presence of palygorskite in the Massive ore is indicative of an arid climate and precipitation from a highly saline, alkaline chemical milieu rich in Si and Mg; the absence of sepiolite is probably due to the availability of Al.

5.3.3. Caliche

The blanket reef (Plate 7A) overlying the massive ore (Section 2.8.5.) and the unconsolidated nodular ore situated between the blanket reef and the massive ore (Section 2.8.5.) and on and immediately below the surface in other areas (Section 2.8.4.) both appear to be manifestations of caliche (calcrete) accumulations. Textural evidence indicates that the blanket reef forms by the replacement (Plate 7D) and cementation of earlier formed magnesite nodules and that the nodular ore represents an early stage in the

........../ development

development of the blanket reef.

According to REEVES (1970) massive caliche may form under semi-arid conditions on rapidly aggrading near-surface carbonate rocks. Ideally the climate should be neither arid nor humid : too little water allows only surficial accumulations of carbonate, while too much causes leaching of the solubles. The process is effected by the downward transportation of upper zone solubles followed by precipitation as a result of evapo-transpiration, some underlying solubles initially rising with capillary water.

ARISTARAIN (1970) has shown that Ca, C, O, H, Mg, S, Fe^{3+}, Si and Ti are concentrated in the upper parts of the caliche horizon, their abundances decreasing with depth and that Ca, C, O and H are concentrated relative to the other elements. GOUDIE (1972) postulates that the accumulation of Ca relative to Mg is probably due to the greater solubility of the latter and also possibly because Mg is removed from the soil pore water by cation exchange on clay minerals.

Thus, the evidence suggests that the blanket reef and nodular ore are formed by the surface weathering of the massive ore under the influence of downward percolating water in semi-arid climates.

5.4. Summary

Slightly acid, oxidizing rainwater containing CO_2 in solution effects the alteration of the peridotites and pyroxenites at the base of the Bushveld Igneous Complex by hydrolysis. The first minerals to be affected are the olivine in the peridotites, which is

.........../converted .....

converted to chrysotile and magnetite, and the feldspar in both rock types. The pyroxenes and serpentine are subsequently attacked and the first quartz and carbonate crystallises. Oxidation of the iron commences at an early stage and continues throughout the process. Si and small quantities of Al, Mg, Fe^{3+} and Na are removed in solution, while the Ca and C contents of the altered rocks increase relative to the other elements. OH initially increases during serpentinization and the formation of hornblende, which commences crystallization at an early stage, but decreases later during the breakdown of the hydrous minerals. K remains constant, presumably since it is fixed in phlogopite : primary phlogopite remains unaltered during weathering, while secondary phlogopite is observed to form during the middle and late stages. Brugnatellite is a late stage accessory mineral. Preferential leaching of Mg relative to Ca results in the predominance of dolomite over magnesite in the altered rocks.

During rainstorms the soluble constituents Mg, Si, Al, Fe^{3+} and Na are removed in solution, much of which probably reaches the river, but considerable quantities of which are trapped in the soil on the plain below the hill slopes. Subsequent evaporation results in the crystallization of magnesite, dolomite, quartz and palygorskite. Weathering of these deposits by the downward movement of groundwaters lead to the formation of Ca-enriched blanket reef and nodular ore.

During the periods following rainstorms when the soil and surface rocks are saturated or semi-saturated with water, quartz and carbonate collects in openings in the parent rocks, resulting in the formation of the vein, skeletal and zebra ores.

six

economic aspects

6.1. Composition of the Ore

Most of the data pertinent to this Section have been dealt with fully in Chapters 2 and 3 and only the main conclusions will be summarised here.

The massive ore, the only variety of any economic importance as far as size of reserve is concerned, is very uniform, showing little variation laterally or vertically (Section 2.8.5.). The

.........../ impurities ......

impurities decrease slightly with depth but never disappear completely. A comparison between Tables IV and V shows the upgrading effect achieved by hand-cobbing (Section 3.2.1.). Any attempt at finding a method to beneficiate the ore should take into account the finely divided nature of the impurities as well as their identities : dolomite, quartz, magnetite, chromite and palygorskite are the non-magnesite components remaining after hand-cobbing (Section 3.2.). The material removed by cobbing consists of pyroxenite pebbles and boulders, soil, dolomite, opaques, quartz and grains of weathered pyroxene and feldspar (Section 3.3.).

Since the magnesite occurs in flat-lying bodies situated at the surface, opencast mining would be the obvious method of winning the ore; the uppermost 1 - 2 m, consisting of blanket reef, soil and calcareous nodular ore, must be considered as overburden.

6.2. Ore Reserves

Information regarding ore reserves is very contradictory. The conclusions derived as a result of the wagon drilling undertaken by Goldfields of S.A. Ltd. (CLUVER and LAWSON, 1972) (Section 2.8.5.) must be regarded as the most reliable since they are based on the only systematic investigation.

The Goldfields estimate of 5,5 million tons of magnesite was arrived at by calculating an average composition of the bodies delineated by drilling, by analyzing the material taken from the holes in 5-foot lengths and subtracting the non-$MgCO_3$ fraction from the total calculated tonnage.

......./The ......

The average composition estimated by Goldfields is :

$MgCO_3$	33,8%
$CaCO_3$	12,1%
SiO_2	6 - 8%

This may err on the low-grade side as the estimate appears to include the uppermost zone of overburden.

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