Black carbonaceous calcite associated with serpentinite from Oman

BLACK pigmentation in calcite is an uncommon feature, generally caused by manganese oxide inclusions such as hollandite (Hewett and Radtke, 1967), todorokite (Hanold and Weber, 1982; Radtke et al., 1967), and cryptomelane–psilomelane (Aigner, 1975), in which associated silver enrichment is of occasional importance. In the Swabian Alps, the black calcite described by Hanold and Weber also contains up to 0.2% of graphite and quartz as a result of contact metamorphism. Here however, we report an entirely different paragenesis in which the carbon ($\pm$hydrocarbon) is X-ray amorphous, free of manganese oxide and silver, and is derived by low-temperature precipitation in serpentinite.

Environment of formation. The black calcite occurs in a restricted microenvironment in Suaal, a small village area in the interior oasis town of Nizwa, shown as 'N' in Fig. 1. Nizwa lies at the edge of harzburgite foothills which form part of the mantle sequence of the Semail ophiolite nappe (Lippard et al., 1986; Glennie et al., 1974). The harzburgite, together with minor dunite and lherzolite, is a monotonously uniform lithology which varies only in the extent of partial serpentinisation (typically 50 to 80%), and in slight fluctuations in the olivine/pyroxene ratios. This mantle sequence weathers to more complete hydration (i.e. 80 to 100%) in the derived alluvium as it accumulates both in narrow steep-sided wadis which dissect the foothill area, and in the main wadi system which borders the harzburgite.

Although structurally below the mantle sequence, an autochthonous limestone–dolomite anticline rises a few kilometres to the north of Nizwa to form the much higher massif of the 'Jebel Akhdar', whose culmination, at 2000 to 3000 m, is part of the Oman mountain axis. Much of both the massif and foothills drains southwards through Nizwa, thereby yielding both derived sediments, from coarse gravel to clay grade, and perennial groundwater. Overall, Neogene sedimentation flanking the Oman mountains is complex, but a relatively simple stratigraphy exists in Nizwa itself. A composite section, shown in Fig. 2, comprises:

(5) A highly variable subcrop topography of weathered mantle sequence in the form of a porous brown to black friable angular gravel transitional to and overlying less fractured but generally well jointed serpentinite with a thickness measured at least in hundreds of metres.

(4) Isolated pockets of serpentinous conglomerate or soft grey powdery serpentine (precipitated from alkaline groundwaters, as discussed below). This is poorly exposed in the surface environment, and is of unknown thickness.

(3) A fluvial sandy conglomerate largely to entirely consisting of serpentinite clasts obviously derived from (5) above, generally well cemented with calcite or lesser dolomite, and containing thin sand or silt lenses. Multiple cycles of crude cross-bedded and well sorted textures are ubiquitous, with the coarser porous fraction often constituting the most productive aquifer of the section, although the permeability to groundwater is very varied, depending upon both the extent of clay precipitation and carbonate cementation. The thickness is up to 20 m. This unit exhibits an obvious colour zonation, in which the upper facies, corresponding to the unsaturated and upper saturated horizons, is stained pale brown due to weathering under oxidising conditions. At deeper horizons the lower facies are generally unchanged, due to the reducing conditions discussed below, and retain their original blue-grey colour.

(2) Up to 10 m of impure calciferous loess, uniformly fine grained, and capped by a limestone gravel deflation lag.

(1) The modern fluvial channel: a complex of partially sorted and reworked sandy gravel of up to dm sized, predominantly carbonate clasts, with silty lenses and widespread calcrete development both at the surface and at irregular horizons throughout its thickness of about 10 m. These modern sediments are incised into the older sequence. In addition to the main wadi, which drains both the massif and mantle sequence, several important tributaries drain the mantle sequence alone, resulting in contemporaneous low banks and outwash fans of ultramafic conglomerate with slight to moderate carbonate cementation. Superficially the latter sediments are often identical to the older unit 3 conglomerates, and differ only in their degree of cementation. Both the upper and lower
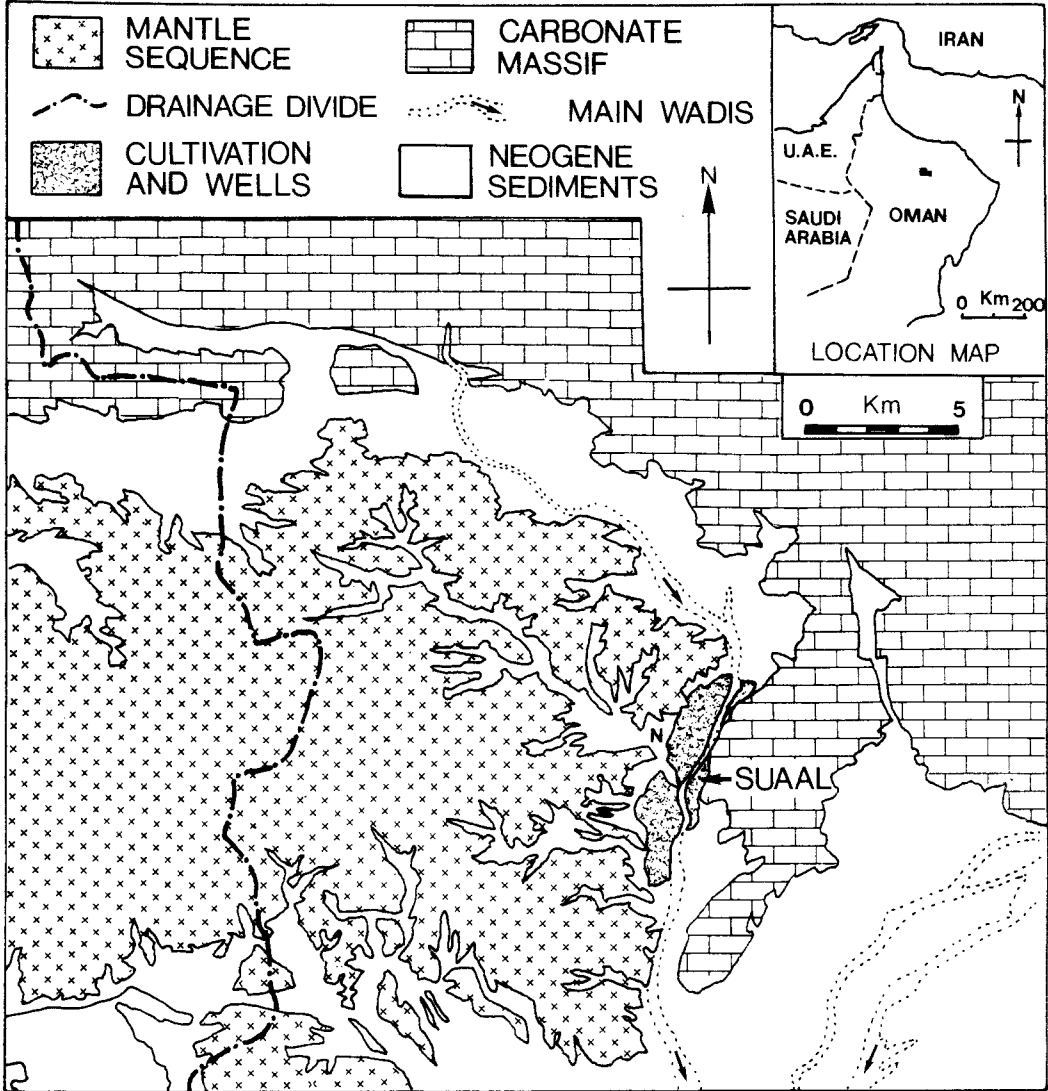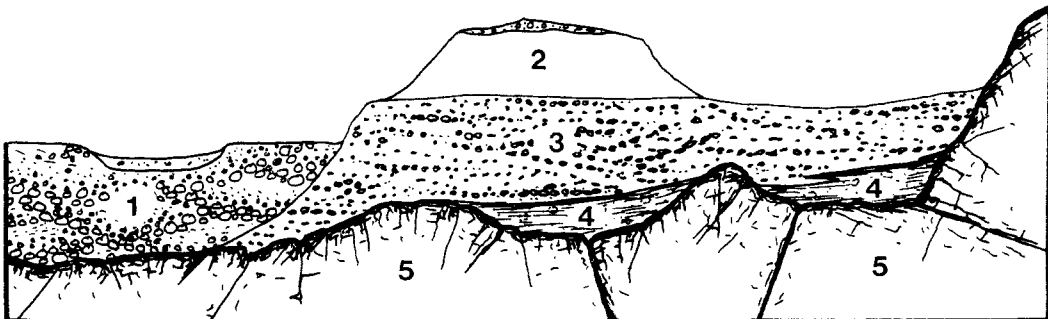
FIG. 1. Geological setting.

FIG. 2. Composite sedimentary section (schematic).

facies of unit 3 may also be present in unit 1 sediments.

Under the semi-arid conditions (mean annual rainfall 185 mm), soil horizons are few and always poorly developed in the form of calcareous silts of low organic and nutrient content. Although Nizwa is an important interior town its total urban area (< 2 km^2) is a small proportion of the total, the remainder being a high-density mosaic of predominantly date palm plantations. Despite the intensive land use, sedimentary sections are abundant in the numerous dug wells throughout the area (averaging about 0.5 irrigation wells per ha, and about 2 domestic wells per ha), whilst intermittent deepening of the wells in productive horizons of 1, 3, 4 and 5 (above) expose unweathered sediment in many recent spoil heaps. Rarely, calcrete horizons within units 1 and 3 create localised perched water-table conditions, but units 1, 3, 4 and 5 are normally in hydraulic continuity, albeit with grossly contrasting permeabilities.

Occurrence and composition. The host rock to the black calcite is the grey precipitated serpentine of 'facies 4' in the above scheme. This occurs both as a massive compact powder and, more commonly, as a relict conglomerate in which the dissolution of clasts up to four or five cm in mean diameter has left a highly carious and fragile 'serpentinite' with a porosity locally exceeding 50%. All the clasts that have escaped dissolution consist of serpentinite of two markedly differing types that occur in approximately equal amounts. The first is hard black partial serpentinite of normal ultramafic alteration type, containing chromite grains and displaying a mesh texture outlined by göethite exsolution. This is clearly derived by fluvial erosion from the main ultramafic foothill area. The second type of 'clast' consists of very pale grey or pink soft powdery nodules, entirely free of inclusions or any alteration texture and which, together with the darker grey matrix material, diffracts as pure serpentine.

The black calcite has crystallised as euhedral open-space precipitates within the cavities, occasionally as sub-mm crystals or crystal aggregates, but more commonly as one to three cm long crystals, with hexagonal prism to basal section ratios of between 2 and 11, and double terminations in simple rhombohedral ($10\bar{1}0$) form. Most crystals are entirely vitreous black and opaque, although opaque grey and colourless transparent varieties are common, with little or no intermediate pigment densities. Two or three of these varieties may alternate in a single crystal in no particular order along the *c*-axis. Microscopically, axial (concentric) pigment zonation is rarely discernible.

The impurities have apparently caused numerous dislocations resulting in: very common twinning with no consistency of twin laws, granular imperfect cleavage ($10\bar{1}1$) surfaces, prism surfaces varying between perfect, and irregular undulations, and occasionally, pseudo-stylolitic sutures between several stages of epitaxial growth. Many crystals also have a frosted or pitted surface from which matrix type powdery serpentine may be ultrasonically removed. Although transparent parts of the crystal facilitated *in situ* microscopic examination of the black pigment, nothing more than nebulous flocculated aggregates could be resolved. In addition to the black calcite, small quantities of subhedral white calcite aggregates were occasionally found coating fractures in the same hand specimen of serpentinite. Such white calcite is the normal form found in other districts of Nizwa and elsewhere in ultramafic-derived sediments.

Chemical examination of the black calcite by energy dispersive X-ray fluorescence indicated a 'normal', low-magnesian calcite composition with a variable amount of impurities comprising silicate (i.e. the powdery grey serpentine), and traces of Pb and Zn scarcely above the detection limit of about 10 ppm. The latter metals probably occur as finely disseminated sulphide, thereby accounting for the release of trace H_2S upon dilute HCl dissolution.

Acid insoluble residues from both the grey and black calcite fractions were thoroughly rinsed, dried at 90 °C and examined by SEM, XRD and C-H-N analysis. Additionally, a thin (< 1 mm) black earthy residue lining some of the serpentinite cavities, and similar to dusty carbonaceous surface deposits in the modern ultramafic conglomerate, was also examined. This residue was mostly smooth but one specimen also exhibited an intersecting complex of curved laminae reminiscent of the göethite exsolution texture of derived serpentine pebbles, and is therefore interpreted as a relict pseudomorph.

All three air-dried residues diffracted as serpentine with a minor clay peak at 13.9 Å. The latter, by analogy with other clays precipitated around the same general horizon elsewhere in the ophiolite, was probably a Mg-rich smectite such as stevensite. No graphite or manganese oxides were detected. The analyses were:

Sample	C%	H%	N%
A: Acid insoluble residue from 100% black calcite	65.80	2.03	1.14
B: Acid insoluble residue from 95% grey calcite	1.43	1.47	0.02
C: Untreated residue lining the serpentinite cavities	3.84	1.32	0.16

Samples B and C consist mostly of serpentine contaminated with a small proportion of black pigment, a conclusion supported by the SEM examinations, which resolved only irregular platelets of presumed lizardite, approximately 10 μm in mean diameter in both samples. Unfortunately in sample A, only platelets in an amorphous matrix could be resolved. The infra-red absorption spectrum of sample A, was also unsatisfactory due to Si–O and O–H stretching band interference from the associated serpentine. However, possible C$=$C and/or C$=$N bonds were suggested by a weak peak at 1620 cm^{-1}. A small C–H (aliphatic?) stretching peak occurred at 2920 cm^{-1}, and a possible N–H stretching peak occurred at 3350 cm^{-1}. There was no indication of 'aromatic' structures.

Differential thermal analysis of sample C yielded a main endothermic peak of between 87 and 155 dg. min. T. g^{-1} at 584.5°. This could correspond to a range of 'high-grade' hydrocarbons but could also be due to an anomalous low-temperature dehydroxylation peak of serpentine. The characteristic endothermic peaks of graphite (about 610 °C) and 'normal' serpentine (600 to 660 °C) were absent, but a small endothermic peak at 810 °C was almost certainly due to the serpentine. Several small but sharp endothermic peaks from about 310 to 370 °C were probably caused by the liberation of volatile matter from organic compounds rich in hyroxyl and other oxygen-containing groups.

Finally, samples A and C were treated with HF followed by HNO$_3$ and aqueous rinses, to remove the silicates, and the carbonaceous residue analysed by mass spectrometer to yield: sample A δ^{13}C $= -19 \pm 1$ per mil with respect to PDB, sample C δ^{13}C $= -22 \pm 1$ per mil with respect to PDB. These values are not generally characteristic of primary mantle carbon and are therefore attributed to contamination of the mantle sequence during initial nappe detachment and emplacement in a deep marine environment when initial basal serpentinisation, and hence reducing conditions, would have been generated.

Process of formation. In view of the Recent sedimentary setting within an actively varying low-temperature (30 to 35 °C) hydrological system, the black calcite precipitation is considered in terms of hydrochemical processes.

Groundwater in the Nizwa district is of two contrasting types, i.e. bicarbonate and hydroxide-dominated chemistries (Gibb *et al.*, 1976; CCEWR, 1986; Stanger, 1986). The bicarbonate groundwaters, which predominate in the near surface sedimentary sequence, vary greatly in their cationic compositions, according to provenance. In particular, the m^{Ca}/m^{Mg} ratio averages 0.36 ($\sigma = 0.19$, $n = 32$) from the weathered mantle sequence as

opposed to 3.2 ($\sigma = 3.0$, $n = 20$) from the carbonate massif and adjacent fanglomerates, with a larger absolute variation of m^{Ca}/m^{Mg} from sediments in Suaal (generally units 3 and 4), of 0.07 to 2.5. In addition to the spatial variation, the hydrochemistry is also influenced by hydrologic parameters since groundwater drainage tends to be faster from the carbonate gravels than from the finer grained ophiolite derived alluvium. In general therefore, the Ca/Mg ratio decreases with time as groundwater recession increases.

Groundwater recharge from flash floods is infrequent, typically two to three times per annum, with the result that surface water is normally absent and groundwater residence times are long. Consequently approximate chemical equilibrium conditions and saturation with respect to the common carbonate minerals predominate throughout the year (cf. Table 1). Slight undersaturation with respect to calcite and dolomite lasts only for a few days or weeks after recharge. Flood recharge is also a high energy process in which aeration and consequently positive redox conditions are generated.

Table 1. Saturation Indices log(IAP/KT)* of various groundwater types from the Suaal district of Nizwa

Mineral	Groundwater type		
	bicarbonate pH 7 to 8	transitional pH about 9	hydroxide pH 11 to 12
Forsterite	-8.2 to-1.0	-2.8 to -0.9	-3.0 to +2.1
Enstatite	-3.1 to 0	-1.3 to +0.4	-1.0 to +1.0
Diopside	-5.0 to -0.6	-0.9 to +2.2	+3.6 to +7.0
Serpentine	-4.7 to +5.5	+2.7 to +6.4	+5.2 to +9.9
Aragonite	-0.5 to +0.7	+0.4 to +0.5	+
Calcite	-0.2 to +0.8	0.7	+
Dolomite	+0.2 to +2.5	+2.1 to +2.7	+

* oversaturation>0>undersaturation

Hydroxide waters are ubiquitous within the underlying fractured mantle sequence. Here the relatively slow-moving groundwaters have reacted with the anhydrous (primary) phases to create $Ca^{2+}/2OH^-$ dominated solutions. These low-temperature serpentinisation reactions have been discussed in detail elsewhere (Neal and Stanger, 1985; CCEWR, 1986; Stanger, 1986) but may be regarded as a stoichiometrically balanced system in which Mg, released to solution by hydration of the olivine (forsterite fraction), reacts with silica, released by the hydration of pyroxenes and the fayalite fraction, to precipitate further serpentine such as that described in '4' above. The Ca^{2+} and

OH^- in solution are derived by dissolution of the minor 'diopside fraction' of the mantle sequence, whilst strongly reducing conditions (Eh -165 to -630 mV) are caused by oxidation of ferrous to ferric iron as a by-product of the 'fayalite' fractional dissolution. This results in the reduction of water itself to release H_2 (Neal and Stanger, 1983), the partial to complete reduction of dissolved species, notably sulphate to sulphide and, due to its high solubility under conditions of pH > 11, an unusually high concentration of dissolved H_2S (up to about 10 mg l^{-1}).

Prior to calcite precipitation, the dissolution of serpentinised harzburgite clasts in preference to the precipitated serpentine matrix apparently had a textural control in which dissolution (at high pH) of the residual anhydrous phases, i.e. olivine and pyroxenes, created zones of high porosity. Subsequently the flow of bicarbonate type water would have been concentrated in these zones, thus promoting selective serpentine dissolution within the derived clasts.

Slow mixing of the two water types, either by diffusion or by dynamic migration of the hydrochemical interface, readily precipitates calcite by bicarbonate–hydroxide reaction. However coprecipitation of serpentine appears, empirically, to require gross supersaturation and hence tends to be restricted to periods of more alkaline conditions (perhaps about pH 10? cf. Table 1). Furthermore, the introduction of small quantities of transition metals, derived by 'upstream' carbonate dissolution, into such an alkaline environment could account for the sulphide inclusions by reactions of the form: $H_2S + X^{2+} + 2OH^- \rightarrow XS + 2H_2O$. Fluctuations in the hydrologic regime can therefore account for the precipitation of calcite $\pm$ serpentine and sulphide impurities.

The question of carbonaceous contamination is more problematic. There are three potential sources of carbon in the system: Firstly, black tarry kerogen is a widespread impurity in upper limestones of the Akhdar massif. The acid-insoluble residues of these limestones also invariably contain fine grained quartz, and are often associated with lesser amounts of clays (chiefly illite). No silica was detected in the aforementioned diffractograms, but under alkaline conditions any residual silica would dissolve, whilst the clay structure is likely to be modified. Therefore only the carbonaceous residue is diagnostic of provenance. The infra-red spectrum of the black calcite insoluble residue was compared with those of 24 carbonates from the Akhdar massif. Despite superficial similarities, all of the limestones showed some degree of diagenetic maturity in the organic residue which was lacking in the black calcite. In particular, the limestone residues differed by ex-

hibiting strong alkyl CH_2 absorption at about 2950 and 2860 cm^{-1}, multiple alkyl vibration at 720 cm^{-1} and sometimes, aromatic 'bending out-of-plane' absorbtion peaks at just less than 800 cm^{-1} (cf. Rouxhet et al., 1980). Thus dissolution of limestone clasts within the serpentine conglomerate does not account for the observed carbonaceous residue. The alternative of in situ carbonate dissolution within the Akhdar massif, followed by 'kerogen' transport, chemical degredation and deposition, requires an implausible degree of selectivity and concentration.

Secondly, although the great majority of analysed groundwaters are free of dissolved organic species (as indicated by UV absorption at 275 nm), the leading edge of flash floods usually accumulate extremely high concentrations of heterogeneous contaminants, both in dissolved and suspended form. Whilst precipitation of organics from this source is conceivable, the process of recharge is so widespread that it is, again, difficult to account for such localised carbonaceous occurrence.

The third and probably most likely potential source is derived from the underlying hyperalkaline groundwater. Most emergent hydroxide groundwater pathways evolve gases comprising H_2, N_2 and small quantities of methane (up to 4.3%) and higher hydrocarbons at concentrations of about 100 v.p.m. (Neal and Stanger, 1983). Although the mechanisms of partial oxidation and/or polymerisation are not known, there is a striking coincidence of slow hydroxide groundwater emergence into a highly localised restricted environment, with the requisite conditions for calcite, serpentine and sulphide co-precipitation. Within this environment a rich flora of sulphate reducing bacteria may also be responsible for hydrocarbon metabolism.

In summary, sediments overlying and/or bordering the Semail mantle sequence provide an environment in which the slow mixing of near-surface bicarbonate with deeper hydroxide groundwaters favours the precipitation of calcite. This example, from Suaal, Nizwa, also exhibits co-precipitation of the contaminants serpentine, carbon/hydrocarbon, and traces of sulphides. These are characteristic of a more intermittent process, active only under restricted conditions of high alkalinity and low redox potential. The black carbonaceous pigment is of uncertain provenance, but its precursor seems likely to have been mobilised along with hydrogen from the underlying mantle sequence. However, the isotopic composition of the carbon is inconsistent with a primary mantle origin, and probably results from syn-tectonic contamination of the mantle sequence during ocean-floor serpentinisation.

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Hentschelite and perloffite from the Spring Creek Copper Mine, South Australia

HENTSCHELITE, $CuFe_2^{3+}(PO_4)_2(OH)_2$, a new member of the lazulite group, was recently described from Reichenbach, Federal Republic of Germany (Sieber *et al.*, 1987). At the same time as the proposal to establish hentschelite as a new species was before the IMA Commission on New Minerals and Mineral Names, a barbosalite-like mineral was discovered on specimens from the Spring Creek Copper Mine, near Wilmington, South Australia. These specimens had been forwarded for identification to one of the authors (W. D. B.) by a local collector, Mr John Toma. The mineral was recognised as a new species, but subsequently confirmed as being hentschelite following advice from the Commission Chairman, Dr Joe Mandarino, and discussions with Professor Ekkehart Tillmanns, one of the authors describing the new species.

This paper presents data on the South Australian occurrence of hentschelite and records the first discovery of perloffite, $Ba(Mn,Fe^{2+})_2Fe_2^{3+}(PO_4)_3(OH)_3$, in Australia, also from the Spring Creek Mine.

Occurrence and appearance. Both hentschelite and perloffite occur as well-formed crystals in cavities lined with colourless quartz crystals in a brecciated quartz–limonite host rock. The two minerals have not been observed together. Associated species in the cavities include cuprite crystals, spongy aggregates and crystalline masses of native copper, together with less abundant malachite and baryte. On perloffite specimens, the quartz may also enclose patches of dark brown glassy material forming partially etched tubules and spheres.

The hentschelite forms lustrous, deep greenish