

Calcium and magnesium hydroxide precipitation from alkaline groundwaters in Oman, and their significance to the process of serpentinization

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ABSTRACT. The occurrence and genesis of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ deposits associated with hyperalkaline groundwater from partly serpentinized ultramafic rocks in Northern Oman is reported. Two types of $\text{Ca}(\text{OH})_2$ deposit are differentiated; crystalline portlandite formed by the evaporation of $\text{Ca}^{2+}-2\text{OH}^-$ spring waters, and a form of amorphous gel, not previously known in nature. The latter is a product of present-day low-temperature serpentinization. $\text{Mg}(\text{OH})_2$ (brucite) in both holocrystalline and gel forms is produced by mixing of $\text{Mg}^{2+}-2\text{HCO}_3^-$ surface waters with a $\text{Ca}^{2+}-2\text{OH}^-$ groundwater in both surface and groundwater environments. These results indicate that significant differences exist between the processes of medium- and low-temperature brucite generation.

BRUCITE, $\text{Mg}(\text{OH})_2$, is a common but minor component of many alpine ultramafic environments and has generally been regarded as a product of forsterite (Mg_2SiO_4) hydration (Bowen and Tuttle, 1949; Yoder, 1952; Hostetler *et al.*, 1966). Though difficult to differentiate optically, it occurs typically in the form of fibrous or microcrystalline intergrowths with serpentine, and frequently exhibits petrofabric evidence of early, i.e. syntectonic genesis (e.g. Hostetler *et al.*, 1966). More recently Barnes *et al.* (1967, 1972, 1978), Barnes and O'Neil (1969), Luce (1971), and Nesbitt and Bricker (1978) have all drawn attention to different aspects of a second, low-temperature phase of serpentinization and brucite generation. The evidence for this is based upon the widespread occurrence of circulating groundwater of meteoric origin which emerges from partly serpentinized ultramafic rocks in the form of highly alkaline $\text{Ca}^{2+}-2\text{OH}^-$ springs. Since the emergent spring waters are over-saturated with respect to both serpentine and brucite, the latter

has been assumed to precipitate in amorphous or microcrystalline form following serpentinization reactions.

Calcium hydroxide is extremely rare, having been reported from only one ultramafic terrain (Derkovic, 1973), then without any detail; it is, however, known as a rare component of other environments (Tilley, 1933; Minguzzi, 1937; Carobbi, 1940; Hentschel, 1961; Bentor *et al.*, 1963; Tuttle and Gittins, 1966; Gross *et al.*, 1967; Nesbitt and Kelly, 1977; Saines *et al.*, 1980; Barnes *et al.*, 1982).

Here a report is given on the new occurrence of magnesium and calcium hydroxide phases and their significance to low-temperature serpentinization reactions from the Northern Oman ultramafic area. One of the calcium hydroxide phases, an amorphous form, has not previously been reported in nature.

Background setting

During a water resources survey (Gibb *et al.*, 1976) and subsequent hydrochemical research, sixty-seven alkaline spring and well waters in rocks throughout the Lower Semail Nappe were examined. The Semail Ophiolite Nappe outcrops over the major part of the Northern Oman mountains, including a small part of the United Arab Emirates, an arc of some 650 km from the Mussandam peninsula in the north to the Jebel Ja-Alan near the easternmost tip of the Arabian peninsula. It represents up to 7 km of oceanic crust and upper mantle material obducted over the Arabian continental edge during the late Cretaceous period (Glennie *et al.* 1974). Most of the springs

are situated within the ultramafic cumulate zone between partially serpentinized harzburgite and the overlying units of the ophiolite. The springs are of a $\text{Ca}^{2+}-2\text{OH}^-$ type having a pH of up to 12.1, and consequently react with CO_2 either directly from the atmosphere or indirectly during mixing with bicarbonate-rich surface waters to precipitate either calcite or aragonite; detailed hydrogeological descriptions will be presented more fully in a later paper.

Chemical and mineralogical analyses

Two hundred and fifty precipitated sediments associated with alkaline groundwaters were investigated by wet chemical and X-ray diffraction by drying at 40°C and grinding, to a particle size of < 5 mm mean spherical diameter, to avoid particle size interference effects (Klug and Alexander, 1974). Samples were mounted on a single silicon crystal, cut to a non-diffracting plane (to avoid high background interference), for diffraction by $\text{Cu-K}\alpha$ radiation. The $\text{Ca}(\text{OH})_2$ gels were diffracted under thin X-ray transparent plastic 'clingfilm' to avoid reaction with atmospheric CO_2 . No analogous precautions were necessary for the brucite gel or portlandite samples since preliminary tests revealed their chemical stability in the atmosphere.

The chemical compositions of the brucite and $\text{Ca}(\text{OH})_2$ gel (Table I) were determined using standard wet chemical techniques. A sedimentation technique was used to remove CaCO_3 contaminants from the brucite phase, though total separation could not be achieved. Nevertheless the results indicate that carbonate ions are incorporated into the brucite phase, since insufficient Ca is present to account for more than two-thirds of the carbonite fraction of the sample. Total carbonate in the sample amounted to 10%.

Analyses of selected vein carbonates for carbon and oxygen isotope ratios ($^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$) were made using a VG Micromass Spectrometer type 602C. The phosphoric acid technique (MacCrea, 1950) was used for the analysis and all the carbonates were assumed to have the same kinetic fractionation factor (1.01025) for CO_2 libera-

tion (Sharma and Clayton, 1965). The isotopic measurements were made relative to Connemara marble as a working standard, and subsequently normalized with respect to the International standards SMOW (for oxygen) and PDB (for carbon).

Calcium and magnesium hydroxide deposits

Portlandite was found at only one location, the Jebel Awq region, at the leading edge of the nappe, where a cluster of alkaline spring seepages emerge from mixed basic/ultramafic cumulates (coordinates: UTM Grid Zone 40, EA 5430, 5230). This occurrence took the form of small white cauliflower-shaped microcrystalline intergrowths of portlandite and calcite, together with halite, which was precipitated along rock surface/joint intersections where the associated seepage outflows were entirely lost by evaporation. Here the presence or absence of portlandite is controlled by the predominance of one of two competing processes. Evaporation of spring water raises the Ca^{2+} and OH^- activities above portlandite saturation level, resulting in its precipitation. This process is counteracted by atmospheric CO_2 absorption by the spring water, resulting in loss of OH^- , and CaCO_3 . Progressive atmospheric reaction results in the spring waters becoming increasingly under-saturated with respect to portlandite since both Ca^{2+} and OH^- activities decrease concomitantly. Portlandite forms from highly alkaline spring waters when the evaporation rate exceeds the CO_2 absorption rate.

Amorphous calcium hydroxide was only observed at a spring in the lower cumulate zone of the ophiolites about $\frac{1}{2}$ km north-east of Karku village (coordinates: UTM Grid zone 40, FA 6069, 5831). Here alkaline groundwater outflow, at about 1 litre min^{-1} , greatly exceeded the potential evaporation rate. $\text{Ca}(\text{OH})_2$, in the form of a grey translucent amorphous gel, accumulated intermittently at the bottom of a small rockpool fed by a nearby spring, and was observed only twice during ten site visits.

The gel deposit was thermodynamically unstable with respect to the spring water. Typical calculated

TABLE I. Chemical analysis of Oman gel deposits (dilute HCl soluble fraction*)

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	OH^-	CO_3^{2-}	$\text{Si}\dagger$
$\text{Mg}(\text{OH})_2$	0.2	<0.1	27.7	4.6	0.1	<0.1	<0.1	36.1	10.5	<0.1
$\text{Ca}(\text{OH})_2$	<0.1	<0.1	<0.1	54.1	<0.1	<0.1	<0.1	45.9	<0.1	<0.5

* Results normalized to 100% by weight.

† Silicate-silicon determined as blue molybdo-silicic acid.

solubility products ($a_{Ca^{2+}} + a_{OH^-}$) were three orders of magnitude lower than the portlandite solubility product of $10^{-5.1}$ at about 23°C (data from Greenburg and Copeland, 1960), where the activities of Ca^{2+} (a_{Ca}) and OH^- (a_{OH}) were calculated according to Plummer *et al.* (1976) using the chemical data given in Table II. In this calculation the activity of the species Mg^{2+} , $MgOH^+$, $MgSO_4^0$, Ca^{2+} , $CaOH^+$, $CaSO_4^0$, Na^+ , $NaSO_4^-$, $Na_2SO_4^0$, $NaCl^0$, KSO_4^- , KCl^0 , SO_4^{2-} and OH^- were obtained using the thermodynamic data collated by Truesdell and Jones (1974).

TABLE II. Alkaline spring water analyses

	Karku (meq l ⁻¹)	Jebel Awq (meq l ⁻¹)
Na ⁺	11.5	35.9
K ⁺	0.27	0.56
Mg ²⁺	0.024	0.0033
Ca ²⁺	3.78	3.08
Cl ⁻	9.67	26.1
SO ₄ ²⁻	0.10	0.27
CO ₃ ²⁻	< 0.001	< 0.001
NO ₃ ⁻	0.05	< 0.01
OH	6.00	11.39
Σcations - Σanions		
Σcations	1.6%	-4.5%
pH	11.57	11.45
Temperature (°C)	23	23

In view of the gross undersaturation and relatively high throughflow of the host solution, the gel must be intermittently flushed out of the ultramafic groundwater pathway(s) to settle out under quiescent conditions within the spring chamber. Since the gel is amorphous it must have formed recently, presumably by low-temperature (35°) reactions (Barnes *et al.*, 1978) in a hydrologically active groundwater system. Here either the groundwaters have Ca^{2+} and OH^- concentrations even higher than those observed in the springs or silica impurities have depressed the solubility of the gel (Brunauer *et al.*, 1958). Alternatively but much less likely (since crystalline $Ca(OH)_2$ would be expected to form; Berger and McGregor, 1973) the gel could be a product of pre-existing $Ca(OH)_2$ generated as a byproduct of early, relatively high-temperature serpentinization under highly alkaline conditions (Moody, 1976; Sakai *et al.*, 1979).

Brucite is precipitated in both the wadi channel and spring chamber environments. In the wadi it is sometimes co-precipitated with serpentine and/or aragonite in the mixing zone of the two water types.

In so doing it forms a fine white granular mass which accumulates in deeper, less turbulent parts of the stream bed. Of twenty-one carbonates sampled from the wadi bed, three were found to contain brucite, two of which also contained serpentine. Such discontinuous generation of brucite is to be expected in view of the varying mix proportions of the surface and spring waters, since a relatively high HCO_3^- component would depress the mixed water alkalinity to below saturation level with respect to $Mg(OH)_2$. Brucite gel was found at only three spring sites and in significant quantities at only one of these sites. The main occurrence was at the same spring site where amorphous $Ca(OH)_2$ was found (Karku). Here the brucite occurred, beneath a crystalline calcite film, in the form of a mixed carbonate-brucite gel closely resembling the sludge type deposits of the wadi environment. An analysis of the brucite gel (Table I) differs from previously reported gel analyses from other environments (Barnes and O'Neil, 1969; Luce, 1971) in that magnesium silicate phases are absent.

Since no surface supply of $Mg(OH)_2$ exists in the Karku spring vicinity, the brucite must originate within the ultramafic rock. Superficially, therefore, accumulation of $Mg(OH)_2$ and $CaCO_3$ in the spring environment may be adequately explained by a combination of present-day serpentinization of the ultramafic rocks to produce $Ca^{2+} - 2OH^-$ water and brucite, followed by flushing of brucite from the aquifer to accumulate in the quiescent conditions of the spring chamber. Simultaneously, atmospheric CO_2 generates a surface carbonate film from the OH^- in solution. This model, however, fails to account for the granular carbonate mixed with brucite gel beneath the surface carbonate layer. This difficulty is more apparent from the carbonate stable isotope compositions (Table III) which suggests that the granular carbonate mixed with the gel, and the surface carbonate film, are of

TABLE III. Stable isotope data for carbonates from the $Mg(OH)_2$ -rich pool and from other ultramafic veins at Karku

	$\delta^{13}C^*$	$\delta^{18}O^\dagger$
Surface carbonate film	-23.4	13.8
Granular deposits	-13.5	25.3
Vein dolomites	-7.8	30.6
Vein calcites	-7.1	26.4
	-9.2	28.1
	-15.8	27.7

* Per mille deviation with respect to PDP.

† Per mille deviation with respect to SMOW.

differing origin. Furthermore, the close similarity in texture and isotopic compositions between granular carbonates of mixed water provenance ($\delta^{13}\text{C} - 12.7$; $\delta^{18}\text{O} + 27.7$) and rock pool provenance ($\delta^{13}\text{C} - 13.48$; $\delta^{18}\text{O} + 25.3$), strongly suggests a comparable origin; the markedly different stable isotope composition for the platelets ($\delta^{13}\text{C} - 23.35$; $\delta^{18}\text{O} + 13.8$) reflects isotopic fractionation at the pool surface where gas-liquid diffusion processes are important. It is therefore concluded that the brucite-generation mechanism involves mixing of predominantly $\text{Ca}^{2+} - 2\text{OH}^-$ with $\text{Mg}^{2+} - 2\text{HCO}_3^-$ type waters within the ultramafic rock, followed by 'flushing out' of the products $\text{Mg}(\text{OH})_2$ and CaCO_3 . Support for this mixing model is supplied by four lines of evidence.

1. The common occurrence of secondary calcite, dolomite, and magnesite veins in the ultramafic rocks, especially in some of the basal serpentinites, indicates a carbonate input to the system. Furthermore, oxygen isotope data for vein carbonates (Table IV) and unpublished data for thirty alkaline spring waters ($\delta^{18}\text{O} + 2.0$ to -4.0% with respect to SMOW) indicate formation temperatures between $\sim 30^\circ$ and 60°C (O'Neil *et al.*, 1969; Tarntani *et al.*, 1969; O'Neil and Barnes, 1971, as modified by Friedman and O'Neil, 1977).

TABLE IV. *Brucite analyses*

	1	2	Pure $\text{Mg}(\text{OH})_2$
MgO	68.42	60.38	69.10
Na_2O	0.34	—	0.00
BaO	0.11	—	0.00
FeO	0.00	8.74	0.00
H_2O	30.98	30.88	30.88
Σ	99.85	100.00	100.00

Sample 1. Water clear, coarsely crystalline aggregates from serpentinite/metasedimentary mélange, Minabak, Oman. Al_2O_3 , MnO, K_2O , P_2O_5 , S, CaO, and NiO were all less than detection limit of 0.01 wt. % (by energy dispersive X-ray fluorescence).

Sample 2. Analysis based on Shtynberg and Chachuklin (1969) data. FeO component calculated as the mean of fourteen brucite samples ($\sigma = 3.4$ wt. %).

2. Monitoring of the Karku spring water chemistry over a period of about three years has indicated that recharge from large but infrequent rainstorms has depressed the spring water pH to between 7 and 8, i.e. similar to normal surface waters. Subsequent drought has resulted in reversal of the spring-water chemistries to more normal alkaline conditions. Therefore, at least part of the

ultramafic aquifer is occasionally recharged with wadi water.

3. Millimetre-thick compound veins of pale-green serpentine and calcite are commonly found cross-cutting the serpentine. They obviously constitute the present fluid pathways and clearly post-date the early phase(s) of pervasive partial serpentinization. Late-stage precipitation reactions must therefore involve secondary serpentinization.

4. A prominent vein of brucite, coated with precipitated serpentine, was found at the basal thrust of the ultramafic rock. This thrust zone is an important groundwater pathway at the interface between the ophiolite and underlying sediments and therefore constitutes the optimum environment for mixing of $\text{OH}^-/\text{HCO}_3^-$ groundwaters. The brucite takes the form of exceptionally pure, transparent euhedral aggregates of Mg end-member composition (Table IV) in contrast to the relatively Fe-enriched *in situ* brucite normally found intergrown with earlier, higher temperature, phases of serpentine (Hostetler *et al.*, 1966).

Conclusions

If present-day serpentinization reactions are volumetrically significant, then it is important that the reactions involved should be viewed in terms of an open system in which $\text{HCO}_3^- - \text{Mg}^{2+}$ -dissolved silica, and $\text{Ca}^{2+} - \text{OH}^-$ are the input and output components respectively, rather than with emphasis being placed upon simple hydration reactions. Furthermore a distinction should be made between initial pervasive serpentinization involving the hydration of olivine and pyroxene to give 'alteration' serpentine \pm brucite, and later serpentinization involving the precipitation of serpentine and brucite from mixed groundwater types. The evidence from this study and other workers (Glennie *et al.*, 1974; Barnes *et al.*, 1978) suggests that both high- and low-temperature serpentinization of the Oman ultramafic rocks has taken place. In common with previous studies (Campbell, 1975) the relative extent of low-temperature serpentinization is obscure. Whereas the ultramafic rock contains abundant petrofabric evidence of dominantly syntectonic (i.e. relatively high-temperature) serpentinization, a significant fraction, of the order of 10%, of low-temperature facies serpentine is estimated to occur in sediments derived by erosion of the ultramafic rock.

The ground and surface water model proposed here for the generation of brucite may be of importance beyond the Oman region since analogous carbonate sludges have been observed elsewhere (O'Neil and Barnes, 1971). An additional process may also apply where initial $\text{Mg}^{2+} -$

2HCO_3^- waters evolve within the ultramafic rock to give $\text{Ca}^{2+}-2\text{OH}^-$ type waters by direct water-rock reaction. Whichever process predominates, Mg^{2+} , HCO_3^- , and dissolved silica in circulating water must be lost from solution during mixing/reaction, thereby providing an explanation for both our results and the Si-Mg gels reported by Luce (1971) and Barnes *et al.* (1972) from springs in the USA.

Whether brucite forms by low-temperature water-rock reaction or by mixing of OH^- - HCO_3^- waters, the end-product is generated under alkaline conditions, which precludes the inclusion of iron into the lattice. Consequently, the presence or absence of iron in brucite from ultramafic rocks provides a criterion for differentiation between high- and low-temperature serpentinization respectively.

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