

THE STABILITY OF BRUCITE IN THE WEATHERING ZONE OF THE NEW IDRIA SERPENTINITE

by

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ABSTRACT

PETROGRAPHIC studies have shown that brucite is a major constituent of the New Idria serpentinite and of the short-fiber asbestos deposit associated with it. Acid-leaching data suggest that the serpentinite averages 7–8 weight per cent brucite, which contains approximately 15 mole per cent “Fe(OH)₂”. Unit cell parameters and electron probe analysis suggest an empirical formula close to (Mg₁₀Fe₂)(OH)₂₄ for this phase. Brucite formed during the initial serpentinization of an olivine-rich parent and is concentrated today in the hard, dense serpentinite fragments scattered throughout a highly sheared matrix of soft, friable asbestos. Although brucite is abundant in the fresh serpentinite it is almost absent from the surface weathering zone, which persists to a depth of 20–30 ft across the entire body. Here, serpentinite fragments have oxidized and brucite has transformed *in situ* into pyroaurite [Mg₆Fe₂CO₃(OH)₁₆·4H₂O] and a new mineral, coalingite [Mg₁₀Fe₂CO₃(OH)₂₄·2H₂O]. Brucite in the matrix material has dissolved in the CO₂-rich ground waters, yielding soluble magnesium ions and amorphous iron oxides which discolor the surface asbestos.

In the laboratory, samples of fresh serpentinite oxidized and disintegrated completely when exposed to the atmosphere for a few months, due to the brucite-coalingite transformation. In the presence of O₂ and CO₂, brucite dissolved completely from a water slurry of the serpentinite, yielding a dark brown residue and a clear filtrate which later precipitated hydromagnesite [Mg₄(OH)₂(CO₃)₃·3H₂O]. These data indicate that in the relatively impervious environment of the residual serpentinite “boulders”, iron-rich brucite oxidizes in air, picking up CO₂ and H₂O to form coalingite. In the presence of excess ground waters, brucite in the friable matrix dissolves, leaving behind a residue of amorphous iron oxides. Dissolved magnesium ions later precipitate as hydromagnesite, which is also abundant in the surface weathering zone of the serpentinite.

INTRODUCTION

AS PART of an over-all mineralogical study of the short fiber asbestos deposits in the southeastern part of the New Idria serpentinite, the stability of brucite in the surface weathering zone of this body has been examined in some detail. Although the serpentinite itself is composed primarily of minerals of the serpentine group, brucite makes up about 7–8 weight per cent of the entire body. It is essentially absent, however, from the surface weathering

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zone, where it has been replaced by dark-colored oxidation products, such as pyroaurite, amorphous iron oxides and coalingite, a new mineral. The present report describes the occurrence of brucite in the fresh serpentinite, and of its reaction products in the surface weathering zone. It also presents possible mechanisms for the oxidation and decomposition of this phase, based upon a combination of field and laboratory evidence.

EXPERIMENTAL

All X-ray diffraction studies were made with either a Norelco High Angle Diffractometer or a 114.6 mm diameter powder camera, using Ni-filtered Cu *K* α radiation. Petrographic examinations were carried out on standard research model polarizing microscopes. The electron probe analyses were made with Associated Electrical Industries apparatus, with the assistance of Mrs. G. Faulring. Acetic acid-leaching experiments were conducted on more than 150 separate samples using essentially the same technique as described by Hostetler, Coleman, Mumpton and Evans (1966).

OCCURRENCE OF BRUCITE IN THE FRESH SERPENTINITE

The New Idria serpentinite is located in Fresno and San Benito Counties, in the southern end of the Diablo Range, about 35 miles northwest of Coalinga, California. The intrusive lies almost directly along the axis of the Coalinga anticline and forms a body about 5 by 17 miles in size. Its physical appearance is different from that of most other serpentinites, in that it is composed almost entirely of highly sheared and pulverized serpentine, having little strength or coherence. Shearing forces have been so great that in most places it is difficult to collect specimens that do not crumble and disintegrate with a touch. Scattered through the highly sheared, flaky asbestos material, however, are numerous blocks of hard, dense, dark green serpentinite, which vary in size from fractions of an inch to tens of feet in diameter. These materials have apparently withstood the intense deformation which has taken place within the serpentinite, and today, stand out as resistant outcrops or "boulders", surrounded by much softer, friable material.

Although brucite is present in almost all types of material from this deposit, it is most abundant in the hard, dense, serpentinite "boulders", and commonly comprises from 10 to 25 weight per cent of these residuals. Petrographically, brucite occurs as scaly aggregates, intimately associated with serpentine minerals. Light-yellow flakes of brucite, approximately 0.03–0.05 mm in size can be seen intergrown with blue–white serpentine. The coexistence of brucite and serpentine suggests that the original ultramafic rock was composed primarily of olivine, with very little enstatite. Only scattered remnants of the anhydrous parent minerals, however, have been found, and Coleman (1957) was unable to identify more than a few isolated grains of olivine in thin sections of serpentinite rocks from this deposit, testifying to the completeness of the serpentinization process. Secondary brucite, in the

form of tiny veinlets, a few tenths of a millimeter across, have also been noted in many specimens. On the other hand, a number of serpentinite "boulders" have been found completely barren of brucite.

Preliminary studies of many samples indicated that the brucite present is not pure $\text{Mg}(\text{OH})_2$, but that it contains significant quantities of iron in solid solution. All attempts at preparing concentrates for chemical analyses failed, however, because brucite could not be completely liberated from the enclosing serpentine matrix. In order to estimate the iron content of typical brucite, a series of acid-leaching experiments was conducted, in which samples of the powdered serpentinite were mixed with dilute acetic acid for several hours at room temperature. The amount of material dissolved by this treatment was considered to be the amount of brucite after correcting for the 1–2% calcite present and the 2–3% of the serpentine in the sample which also dissolves. The Fe/Mg ratios of the leach liquors were used to estimate the amount of iron in the original brucite lattice. As pointed out by Hostetler *et al.* (1966) the Fe/Mg ratios obtained are influenced by several factors, including the amount and the solubility of the serpentine polymorphs present in the sample, the iron content of these polymorphs and the particle size of the original sample. Although the data cannot be used quantitatively, over one hundred drill hole samples from this deposit yielded Fe/(Fe+Mg) values between 10 and 20 atomic per cent, strongly suggesting that the brucite is iron-rich, containing about 15 mole per cent " $\text{Fe}(\text{OH})_2$ ".

Electron probe data, reported in an earlier paper (Mumpton, Jaffe and Thompson, 1965) have verified these results. Brucite grains from several serpentinite fragments were found to contain between 15 and 18 weight per cent Fe, corresponding to approximately the same value mentioned above. Hostetler, Coleman, Mumpton and Evans (1966) supported these results with both leaching data and electron probe analyses. Large variations in the iron content were observed by the probe technique, however, suggesting considerable reworking of the serpentinite body since its formation.

The ferruginous nature of brucite has also been corroborated by the results of film X-ray diffraction studies. In Table 1, d values for a brucite concentrate from this deposit are compared with those of reagent grade $\text{Mg}(\text{OH})_2$ and the $\text{Fe}(\text{OH})_2$ of Bernal *et al.* (1959). The spacings of the New Idria material are shifted slightly towards those of its iron analogue. Assuming a straight line relation between the two end members, an iron content can be calculated for each reflection. The values obtained, between 10 and 17 mole per cent $\text{Fe}(\text{OH})_2$, lend credence to the results of electron probe and acid leaching discussed above.

MINERALOGY OF THE SURFACE WEATHERING ZONE

The surface weathering zone of the New Idria serpentinite extends to a depth of 20–30 ft and covers the entire body. It is characterized by a reddish-brown color and contrasts vividly with the greenish-white asbestos

TABLE 1.—X-RAY DIFFRACTION DATA FOR IRON-RICH BRUCITE FROM THE NEW IDRIA SERPENTINITE

(hkl)	(1) Mg(OH) ₂ synthetic ⁽¹⁾ <i>d</i> (Å)	(2) Brucite Con. New Idria <i>d</i> (Å) I/I ₀	(3) Fe(OH) ₂ synthetic ⁽²⁾ <i>d</i> (Å)	(4) Calculated ⁽⁴⁾ mole per cent Fe(OH) ₂ in (2)	(5) Hypothetical <i>d</i> spacings ⁽⁵⁾ for (Mg ₁₀ Fe ₂)(OH) ₂₄
001	4.770	4.74 70	4.597	17.34	4.741
100	2.725	2.74 10	2.817	16.30	2.740
101	2.365	2.36 100	2.403	Neg.	2.371
102	1.794	1.792 60	1.782	16.67	1.792
110	1.573	1.579 40	1.629	10.71	1.582
111	1.494	1.499 20	1.535	12.20	1.501
103	1.373	1.369 20	1.349	16.67	1.369
200	1.363	n.d. ⁽³⁾ —	1.411	—	1.371
201	1.310	1.314 20	1.349	10.26	1.3165
004	1.192	n.d. —	1.148	—	1.185
202	1.183	1.186 20	1.203	15.00	1.1863
113	1.118	n.d. —	1.115	—	1.1175
104	1.092	n.d. —	1.067	—	1.088
203	1.034	1.034 10	1.040	0.00	1.035
210	1.030	n.d. —	1.067	—	1.036
211	1.0067	1.011 10	1.040	13.03	1.012
005	0.9543	n.d. —	0.923	—	0.9491
114	0.9503	n.d. —	0.941	—	0.9488
212	0.9455	0.949 30B	0.968	15.56	0.9482
300	0.9085	0.912 5	0.941	10.77	0.9139

1. Swanson *et al.* (1956) (A.S.T.M. Card 7-239).

2. Bernal *et al.* (1959) (A.S.T.M. Card 13-89).

3. n.d. = not recorded.

4. Calculated by $\frac{(1) - (2)}{(1) - (3)} \times 100$.

5. *d* values calculated from end member data assuming 16.67 mole per cent Fe(OH)₂.

ore underlying it. In this zone hard, dense blocks of residual serpentinite have been transformed into soft, crumbly, red brown masses; whereas the surrounding friable asbestos material has been only slightly discolored. Many of the surfaces of the "boulders" are coated with rosettes of artinite [Mg₂(OH)₂CO₃·3H₂O] and veinlets of hydromagnesite [Mg₄(OH)₂(CO₃)₃·3H₂O] and aragonite are not uncommon in highly fractured portions of the deposit. One of the most striking features of the weathering zone is the local concentration of hydromagnesite occurring immediately above the water table. Here, pea-size concretions of the hydrous magnesium carbonate are scattered throughout a matrix of greenish-white asbestos. Hydromagnesite often comprises as much as 30% of these zones.

The weathered serpentinite "boulders" differ markedly from their fresh counterparts by containing almost no brucite. Pyroaurite [Mg₆Fe₂CO₃(OH)₁₆·4H₂O], coalingite [Mg₁₀Fe₂CO₃(OH)₂₄·2H₂O] and amorphous iron oxides,



FIG. 1. Serpentinite “boulder” after having been exposed to the atmosphere for several months. Note the exfoliated nature of the “boulder” and the soft material that has crumbled away from it.

however, are abundant. Many "boulders" consist of a highly weathered, outer crust, surrounding a relatively fresh, inner core. Petrographic studies by Mumpton, Jaffe and Thompson (1965) have shown that iron-rich brucite transforms directly into coalingite during weathering with iron apparently oxidizing from ferrous to ferric during the process. Weathering is so rapid that large blocks of serpentinite collected from depths of 40–50 ft, crumble and exfoliate almost completely within a few months when they are exposed to the atmosphere (see Fig. 1). Serpentinite blocks occurring within 1 or 2 ft of the surface have transformed into a dark reddish-brown, powdery mass, in which serpentine is the only phase present detectable by X-rays.

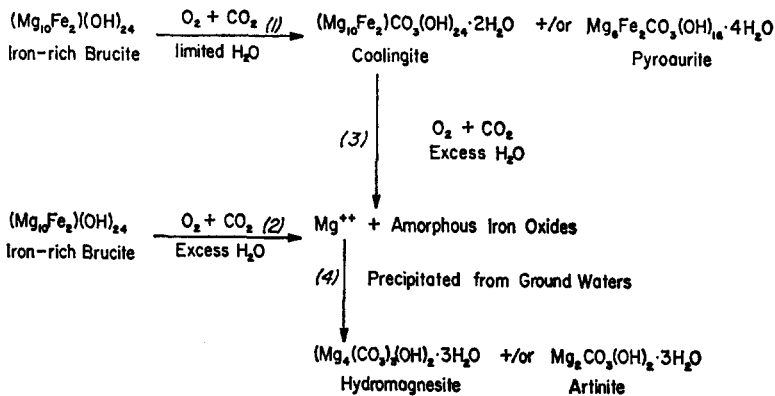


FIG. 2. Oxidation and dissolution reactions of iron-rich brucite.

Although the matrix asbestos material surrounding the serpentinite "boulders" in the weathering zone is light tan in color, no new crystalline phases have been detected. Brucite is generally absent from this material, and apparently has been dissolved by the carbon dioxide-rich ground water which intermittently saturates this part of the deposit, leaving behind a residue of amorphous iron oxide which discolors the matrix material. The magnesium and hydroxyl ions taken into solution apparently react with available CO_2 in ground waters to form the local concentrations of hydromagnesite and artinite discussed above.

LABORATORY STUDIES

Early in the investigation it was noted that many samples of dark green serpentinite rock, which had been collected below the surface oxidation zone, turned brown after having been exposed to the laboratory atmosphere

for several months. X-ray diffraction studies of the dark brown, friable products indicated that the brucite content had diminished considerably, and that coalingite had formed in its place. Powders of other brucite-rich samples also darkened and formed coalingite after having been stored in closed jars for a few months. These results showed that iron-rich brucite is not stable in air, but oxidizes *in situ*, reacting with CO_2 and water vapor to form coalingite and other dark colored products.

Based upon such observations, several brucite-rich serpentinites were exposed to various controlled environments of oxygen and carbon dioxide. In all cases, the gas streams were mixed and bubbled through a water trap to saturate the gas with water vapor. The gas was passed over a packed X-ray holder of a dry powdered sample and then through a stirred water slurry of the same serpentinite sample. Periodically both the dry sample and the slurried material were examined by X-ray diffraction techniques and the phases present identified. The changes in mineral content were estimated by intensity measurements of characteristic X-ray peaks and, although quantitative estimates are not claimed, the appearance or disappearance of individual phases could easily be detected by this method. For almost all studies, a brucite-rich serpentinite (487-52-7) described in detail by Mumpton, Jaffe and Thompson (1965) was used as starting material. This sample was estimated, by acid leaching tests, to contain approximately 25 weight per cent brucite. Experimental results are listed in Table 2.

Under standard laboratory conditions weak reflections of coalingite were observed in the X-ray diffraction pattern of this material after a period of 6 months, during which the surface of the sample turned to a light tan color. This same sample turned brown and formed coalingite after only 5 days when exposed to an atmosphere of moist oxygen and carbon dioxide. With continued treatment, however, coalingite also disappeared, yielding nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and probably more iron oxides after 16 days. Under identical conditions reagent grade $\text{Mg}(\text{OH})_2$ also yielded nesquehonite in 3 days. The water slurry of this same sample changed from a grey-green color to dark brown in only fifteen minutes. At the end of 24 hr the slurry was filtered and dried. The dark brown residue contained no brucite nor any other crystalline phase other than the original serpentine. Upon evaporation, the clear filtrate yielded a white, fluffy precipitate of hydromagnesite. These results suggest that in a relatively dry environment, brucite transforms directly into coalingite by reacting with CO_2 , O_2 and water vapor, while in the presence of excess water and CO_2 it dissolves completely, yielding soluble magnesium ions and dark-brown, amorphous iron oxides which discolor the serpentine residue.

When reacted with moist oxygen alone, both the dry powder and the water slurry formed traces of coalingite in about 50 days. Since carbon dioxide was not introduced into this reaction, no explanation can be offered, since coalingite is a CO_2 -containing mineral. It is possible that some carbon dioxide was obtained from the trace quantities of calcite in the original

TABLE 2.—LABORATORY REACTIONS OF IRON-RICH BRUCITE FROM THE NEW IDRIA SERPENTINITE

Experiment	Starting material	Sample preparation	Gas environment	Time period	Products ⁽⁴⁾	Color
I	Serpentine + Brucite ⁽¹⁾	Dry Mount	Lab. Atmosphere	6 months	Serpentine + s. Coalingite + s. Brucite	Tan
II	Serpentine + Brucite	Slurry	O ₂ + CO ₂ ⁽³⁾	1 hour	Serpentine (+ Hydromagnesite precipitate from solution) ⁽⁵⁾	Brown
III	Serpentine + Brucite	Dry Mount	O ₂ + CO ₂ + H ₂ O	5 days	Serpentine + s. Coalingite	Brown
IV	Reagent Grade Brucite	Dry Mount	O ₂ + CO ₂ + H ₂ O	16 days	Serpentine + Nesquehonite	Brown
V	Serpentine + Brucite	Slurry	O ₂ + CO ₂ + H ₂ O	3 days	Nesquehonite	Gray
VI	Serpentine + Brucite	Dry Mount	O ₂ + H ₂ O	50 days	Serpentine + tr. Coalingite	Tan
VII	Serpentine + Brucite	Slurry	CO ₂	50 days	Serpentine + tr. Coalingite	Tan
VIII	Coalingite concentrate	Slurry	CO ₂	1 hour	Serpentine	Olive-green
				18 hours	Amorphous (+ Hydromagnesite precipitate from solution) ⁽⁵⁾	Red-brown

1. Sample 487-52-7, about 25% brucite, powdered, magnetite removed.

2. Packed into an X-ray holder.

3. Gases bubbled through a water trap and then onto the dry sample or into the water slurry.

4. Identified by X-ray diffraction technique, s = some; tr. = trace.

5. The clear filtrates were heated for about 1 hr; a white fluffy precipitate of hydromagnesite then formed.

sample. It is also possible that small amounts of CO₂ actually entered this basic system from the atmosphere. When only carbon dioxide was bubbled through the water slurry, it turned olive green in a few hours. After 24 hr, the filtered residue showed no trace of brucite and only serpentine could be detected in the X-ray diffraction pattern. In the absence of oxygen, it is possible that the dissolution of brucite yielded an amorphous residue of *ferrous* oxides, rather than *ferric* oxides produced when oxygen was present.

DISCUSSION AND CONCLUSIONS

From the field observations and the laboratory experiments discussed above, a number of conclusions regarding the occurrence and stability of brucite in the weathering zone of the New Idria serpentinite can be drawn. First of all, iron-rich brucite having the general formula $(\text{Mg}_{10}\text{Fe}_2)(\text{OH})_{24}$ is a major constituent of the fresh, unweathered serpentinite. It is much more abundant in the hard, dense blocks of residual serpentinite than in the soft, friable asbestos material surrounding them. The surface weathering zone of the deposit is characterized by the absence of brucite and the presence of brown-colored products such as pyroaurite and coalingite. This zone is saturated with CO₂-charged ground waters, which percolate freely within the friable asbestos material. Here brucite has been dissolved, leaving behind a dark-brown residue of oxidized, amorphous iron oxides, which discolor the matrix asbestos. Soluble magnesium ions later precipitated from the ground waters in the form of the hydrous magnesium carbonates, hydromagnesite and artinite. Zones of the hydromagnesite are common throughout the deposit, immediately above the water table.

The relatively impervious nature of the hard, dense serpentinite "boulders" apparently limits the passage of ground waters, and consequently little dissolution has taken place. Iron-rich brucite, however, is oxidized and converted *in situ* to coalingite and pyroaurite. Many of the residual blocks show all stages of oxidation, from a highly weathered outer crust, which readily exfoliates upon standing, to a relatively fresh, inner core which still contains brucite in the unoxidized state. In the upper few feet of the weathering zone, such "boulders" are almost completely disintegrated, and here brucite has dissolved completely, leaving only amorphous iron oxide behind. Generalized reactions involving the oxidation and dissolution of iron-rich brucite are shown schematically in Fig. 2.

Hostetler, Coleman, Mumpton and Evans (1966) have noted that in areas of intense shearing or fracturing, brucite is noticeably absent from serpentinite bodies. The lower brucite content of the soft, friable asbestos material beneath the surface weathering zone in the New Idria deposit, compared with the hard, dense serpentinite residuals, may possibly be the result of partial dissolution of this phase by ground waters during the tectonic history of the deposit.

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REFERENCES

- BERNAL, J. D., DAGUPTA, D. R., and MACKAY, A. L. (1959) The oxides and hydroxides of iron and their structural interrelations: *Clay Min. Bull.* **4**, 15-30.
- COLEMAN, R. G. (1957) Mineralogy and petrology of the New Idria District, California Ph.D. Thesis, Stanford Univ., University Microfilms Publ. 21, 266.
- HOSTELER, P. B., COLEMAN, R. G., MUMPTON, F. A., and EVANS, B. W. (1966) Brucite in Alpine serpentinites: *Amer. Min.* (in press).
- MUMPTON, F. A., JAFFE, H. W., and THOMPSON, C. S. (1965) Coalingite, a new mineral from the New Idria serpentinite, Fresno and San Benito Counties, California: *Amer. Min.* **50**, 1893-1913.
- SWANSON, H. E., GILFRICH, N. T., and COOK, M. I. (1956) Standard X-ray diffraction patterns: *Nat. Bur. Stand. Circ.* **539**, **6**, 30.