The mineralogy and chemistry of the nickel carbonates

By T. Isaacs, B.A., M.S., Ph.D.

Department of Geology, The University, Sheffield

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Summary. Nickel carbonate occurs in nature as a hexahydrate (hellyerite) and as a hydroxyhydrate (zaratite), but the anhydrous species is only known as an artificial product. All of the compounds show anomalous properties that have led to confusion in the literature.

Only the calcite structure was found for $NiCO_3$; hydrothermal conditions appear to be essential for its synthesis, and a variation in cell size was found with changes in duration or temperature of synthesis, or both.

Hellyerite probably is $[Ni(H_2O)_6]\,CO_3$, which would explain its ease of decomposition and rarity in nature. Zaratite is not a single mineral, but a composite of amorphous and fibrous components. The conditions under which $NiCO_3$ might be expected to occur are discussed. Nickel bicarbonate formed in the reactions to produce $NiCO_3$; its X-ray diffraction pattern, indicating cubic symmetry, analysis, and optical properties are given.

The behaviour of nickel in these compounds is best explained in terms of crystal field theory.

MOST of the divalent metals that are of sufficient abundance in nature to form well-defined minerals can occur in the form of an anhydrous carbonate, $M''CO_3$; where the radius of the metallic ion lies within the range 0·65 to 0·99 Å, the crystal structure is of the calcite type. A prominent exception is nickel, which, although $NiCO_3$ has been made synthetically, has never been found as a natural mineral in the form of an anhydrous carbonate. Yet nickel is moderately abundant in the crust of the earth, and its ionic radius falls within the limits for a calcite-type carbonate. Rather, it occurs either as a hexahydrate (hellyerite) or as a hydroxyhydrate (zaratite). Where nickel has been observed in association with calcite or dolomite, there are found distinct nickel minerals, which have a composition dependent upon the impurities in the host rock and the compositions of the solutions, rather than a solid solution of nickel in the carbonate.[1]

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[1] A calcite containing 0·65% Ni has been reported (Maksimović and Stupar, 1953) and also one containing 0·83% Ni (Maksimović, 1952). The mineral, zeyringite, has been classed as a calcareous sinter (probably aragonite) containing nickel, but has recently been shown to be aragonite coloured by inclusions of aurichalcite (Meixner, 1962).

The present theoretical and experimental studies indicate explanations for the absence of an anhydrous nickel carbonate in nature, and the modes of formation of the naturally occurring hexahydrate and hydroxyhydrate of nickel carbonate.

Anhydrous nickel carbonate

The compound $NiCO_3$ was obtained in the form of small, emerald green crystals. The morphology of these crystals generally was poor, but a few well-formed rhombohedra were present. Intergrowths were common, some of which may have been twins. Chemical analysis (table I) confirmed a 1:1 molar ratio of NiO to CO_2. It was found that this compound did not dissolve at any appreciable rate in mineral acids (cf. Sénarmont, 1850, and Bizette and Langlès, 1950).

TABLE I. Results of chemical analyses (by weight %)

Sample	NiO	CO_2	H_2O
$NiCO_3$ (smallest cell)	62·8	37·1	—
$NiCO_3$ (smallest cell)*	62·7	37·3	—
$NiCO_3$ (largest cell)	63·3	33·7	2·9
Synthetic zaratite	58·5	15·2	26·9
$Ni(HCO_3)_2$	39·6	49·3	11·0

* from DTA.

TABLE II. X-ray diffraction data for $NiCO_3$ (smallest cell) Cu-$K\alpha$, $\lambda = 1{\cdot}5405$ Å, Ni filter

d_{obs}	d_{calc}	*hkil*	I/I_0	d_{obs}	d_{calc}	*hkil*	I/I_0
3·5077	3·5019	$10\bar{1}2$	48	1·3274	1·3270	$63\bar{9}0$	14
2·9916	—	—	2 B	1·2270	1·2271	$0.0.\bar{0}.12$	5
2·7040	2·7028	$10\bar{1}4$	100	1·2239	1·2238	$21\bar{3}7$	3
2·3001	2·2985	$11\bar{2}1$	27	1·1836	1·1838	$0.2.\bar{2}.10$	2
2·1508	—	—	5 B	1·1651	1·1649	$12\bar{3}8$	6
2·0828	2·0815	$11\bar{2}3$	34	1·1493	1·1493	$22\bar{4}0$	1
1·9224	1·9216	$20\bar{2}2$	28	1·0825	1·0825	$1.1.\bar{2}.12$	4
1·7511	1·7510	$02\bar{2}4$	15	1·0577	1·0576	$13\bar{4}4$	4
1·6780	1·6776	$11\bar{2}6$	43	1·0524	1·0524	$2.1.\bar{3}.10$	3
1·6715	1·6707	$01\bar{1}8$	7	1·0408	1·0408	$22\bar{4}6$	4
1·4975	1·4969	$21\bar{3}1$	2	0·9999	1·0001	$1.2.\bar{3}.11$	9
1·4746	1·4742	$21\bar{3}2$	17	0·9607	0·9608	$40\bar{4}4$	3
1·3928	1·3929	$21\bar{3}4$	13	0·9468	0·9469	$31\bar{4}8$	5
1·3810	1·3811	$1.0.\bar{1}.10$	3	0·9300	0·9299	$2.0.\bar{2}.14$	1
1·3513	1·3514	$20\bar{2}8$	6	0·9008	0·9009	$3.0.\bar{3}.12$	4
1·3335	1·3329	$11\bar{2}9$	9				

B = broad peak

X-ray studies showed that the cell size varied with the duration of the hydrothermal runs, decreasing with increasing length of time in the bomb until a lower limit was reached, after which time the cell size remained constant. The smallest values for the *a* and *c* dimensions, which were determined from the X-ray data given in table II by use of a least-squares refinement technique on an IBM 704 computor, and the corresponding axial ratios were: $a_{\text{hex}} = 4{\cdot}597 \pm 0{\cdot}002$ Å, $c_{\text{hex}} = 14{\cdot}725 \pm 0{\cdot}002$ Å, $c/a = 3{\cdot}203$; the largest cell observed had: $a_{\text{hex}} = 4{\cdot}609 \pm 0{\cdot}002$ Å, $c_{\text{hex}} = 14{\cdot}737 \pm 0{\cdot}002$ Å, $c/a = 3{\cdot}197$; it will be seen that the decrease in the *a* dimension is approximately three times that in the *c* dimension.

Cell size determinations of other authors as well as those of this paper are as follows: $a_{\text{rhomb}} = 5{\cdot}587$ Å, $\alpha = 48° 38'$ (Pistorius 1959); $a_{\text{rhomb}} = 5{\cdot}60$ Å, $\alpha = 48° 31'$ (Langlès 1952); $a_{\text{rhomb}} = 5{\cdot}57$ Å, $\alpha = 48° 43'$ (Langlès 1952); $a_{\text{rhomb}} = 5{\cdot}55$ Å, $\alpha = 48° 43'$ (Bizette & Langlès 1950); $a_{\text{rhomb}} = 5{\cdot}580$ Å, $\alpha = 48° 40'$, this paper, smallest cell.

Optical examination showed that $NiCO_3$ is uniaxial negative with a large birefringence. The optical properties are an inverse function of the cell size, the indices of refraction increasing with decrease in the *a* and *c* values, from ω $1{\cdot}913 \pm 0{\cdot}003$, ϵ $1{\cdot}692 \pm 0{\cdot}002$ for the largest cell observed to ω $1{\cdot}930 \pm 0{\cdot}003$, ϵ $1{\cdot}721 \pm 0{\cdot}002$. The density also increased with the decrease in cell size; the greatest density observed was 4·388 g/cm^3. The optical properties and X-ray data show that anhydrous nickel carbonate has the calcite structure.

Infra-red studies were conducted on samples from runs of durations varying from 1 week to 6 weeks to determine whether there was water present in the structure. Such water, by being present in the crystals made in the shorter runs, would result in the observed increase in cell size. There was bound water present in the crystals from the shorter runs, the amount decreasing to zero with increasing length of the run. Three patterns are shown in fig. 1. A shifting and broadening of the peak in the 5 μ region is seen with increasing water content. Chemical analysis of the sample containing the greatest amount of water (corresponding to the largest cell size) showed that there was 2·9 % by weight water present (table I). The amount of water could not be determined from the infra-red patterns as this type of quantitative analysis can only be done on liquids, not powders, and no suitable solvent has been found for $NiCO_3$.

Differential thermal analyses were carried out on several samples of $NiCO_3$ to determine the decomposition temperature at 1 atmosphere pressure. At a rate of 4°/min, the decomposition temperature was approximately 300° C (fig. 2). Weight loss determinations made simultaneously showed that there was a 1:1 molar ratio of NiO to CO_2.

Synthesis of $NiCO_3$. Successful syntheses of $NiCO_3$ were carried out by Bizette and Langlès (1950), Langlès (1952), and Pistorius (1959), with Langlès reporting a yellow and a green form, both of which he believed to have calcite-type symmetry. Earlier reported syntheses by Sénarmont (1850, 1851), Ferrari and Colla (1929), Krustinsons (1933), Müller and Luber (1930), and Srebrow (1935) are unconfirmed, and it appears that in most cases the products obtained may well have been nickel hydroxy-chlorides rather than nickel carbonate.

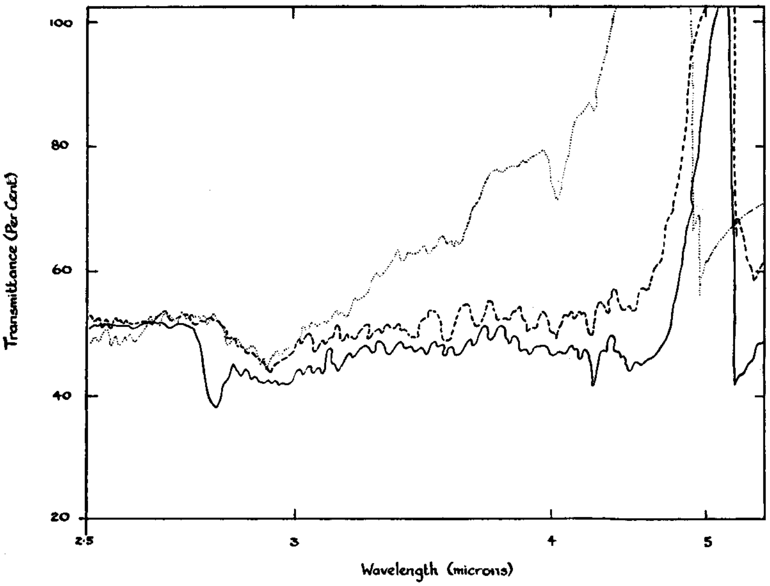

FIG. 1. Infra-red patterns of three samples of $NiCO_3$. The continuous line is the pattern for the sample of smallest cell size, the dashed one for the sample of intermediate cell size, and the dotted one for the sample of largest cell size.

In the present work, the calcite-type $NiCO_3$ was produced by two methods. The first was by the recrystallization of amorphous basic nickel carbonate in a CO_2–H_2O atmosphere at temperatures ranging from 220 to 250° C in Pt-lined Morey bombs. Runs of under 5 days' duration, with insufficient water present, resulted in the formation of nickel bicarbonate rather than nickel carbonate. The reactions were quite slow using this method, time intervals of the order of at least

1 week being required to obtain even finely divided crystalline material. A more satisfactory procedure was to use sodium bicarbonate and nickel chloride as starting materials. Small crystals then could be obtained in a few days, and larger ones suitable for single crystal X-ray studies in runs of 10 weeks' duration. In this second method, it was found that a molar excess of the sodium bicarbonate was required to produce $NiCO_3$ as the sole product; an excess of the nickel chloride favoured the production of nickel hydroxy-chlorides. When other nickel salts were used as starting materials, similar results were obtained.

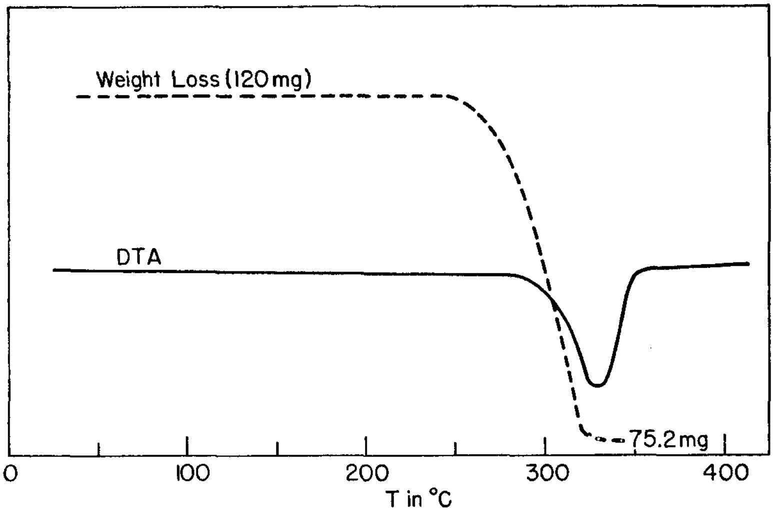

FIG. 2. Differential thermal analysis and weight loss patterns for a sample of $NiCO_3$ with smallest cell size. The pattern was made using a rate of temperature rise of 4°/min.

Attempts to produce $NiCO_3$ by precipitation methods using nickel salts and sodium bicarbonate, sodium carbonate, or potassium bicarbonate were unsuccessful; hydrates of nickel carbonate were the only products formed from these experiments. Heating these hydrates in atmospheres of air or CO_2 produced decomposition rather than the formation of $NiCO_3$.

Experiments were undertaken to simulate possible conditions of formation by geological processes and to investigate the association of secondary nickel minerals with calcite and dolomite. Solutions of nickel sulphate and nickel chloride were added to calcite, magnesite, or dolomite in the presence of CO_2 in a Morey bomb. No anhydrous nickel carbonate was produced in any of these runs, nickel hydroxy-salts being obtained instead.

It is significant that while anhydrous nickel carbonate has never been found as a natural mineral, it can be made with relative ease from zaratite. A sample of natural zaratite was heated to 225° C in a bomb in a CO_2–H_2O atmosphere for two weeks; well-crystallized $NiCO_3$ was obtained.

Langlès' reported yellow form of $NiCO_3$ was never obtained in any of the experiments of this paper. A modification by Firestone (personal communication) of Langlès' method of synthesis was tried, but it too failed to produce this form. We conclude, therefore, that there is only one form of $NiCO_3$. Examination of the X-ray powder patterns given by Langlès (1952) show that both his yellow and green forms are calcite-type, the difference between them being cell dimensions and grain size. The yellow form was made at lower temperatures than the green one. Langlès apparently obtained the same results as those of this paper, that is, the inverse relationship between temperature or time of the run and cell size. Higher temperatures or longer runs will anneal out imperfections.

Studies of possible natural relationships. As there are no reliable thermodynamic data available on $NiCO_3$, the decomposition pressures and corresponding temperatures were determined experimentally. The simple squeezer high-pressure apparatus was used for these studies,[1] because of the low temperature of decomposition of this compound. Table III gives the results of these runs and fig. 3 is an approximate P–T diagram.

Because of the apparent absence of anhydrous nickel carbonate in natural rocks, experiments were conducted to determine whether solid solutions could be formed between $NiCO_3$ and the two most frequently occurring natural carbonates, calcite and magnesite. Two techniques were used: the first was to react solutions of salts of the metals with sodium bicarbonate in a CO_2–H_2O atmosphere in a Morey bomb at 250° C; the second was to make dry mixes of the carbonates in the ratios

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[1] The results obtained using this method could not be quantitative because of the limitations of the apparatus. Two faults could produce anomalous results: one is the possibility of an imperfect seal allowing leakage; the other is the possibility of an imperfect surface line of the pistons resulting in incorrect pressures. Because of these difficulties, replicate runs were made at a few points as a check. But semi-quantitative results were sufficient for the purposes of this work.

TABLE III. List of runs to determine the decomposition temperatures and pressures of $NiCO_3$

Temp. (° C)	Pressure (kilobars)	Results	Temp. (° C)	Pressure (kilobars)	Results
400	10	$NiCO_3$	600	15	NiO
400	12	NiO	600	18	NiO
400	15	$NiCO_3$	600	20	NiO+$NiCO_3$
450	20	$NiCO_3$	600	20	NiO+$NiCO_3$
500	8	NiO	600	20	NiO+$NiCO_3$
500	12	NiO	600	22	$NiCO_3$+NiO
500	14	NiO	600	22	$NiCO_3$
500	15	$NiCO_3$+NiO	625	20	$NiCO_3$+tr. NiO
500	17	$NiCO_3^3$+NiO	650	20	NiO+$NiCO_3$
500	20	$NiCO_3$	700	15	NiO
525	10	NiO+$NiCO_3$	700	18	NiO
550	15	$NiCO_3$	700	22	NiO+tr. $NiCO_3$
550	20	$NiCO_3$	700	25	$NiCO_3$+tr. NiO
550	20	$NiCO_3$	700	27	$NiCO_3$+tr. NiO

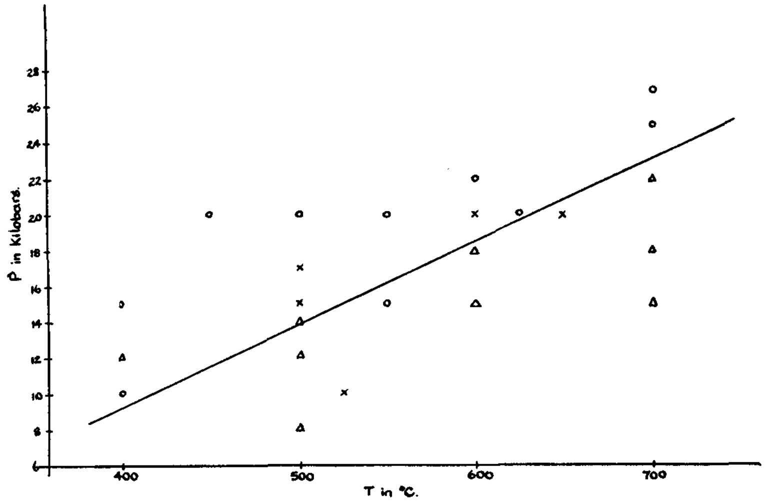

FIG. 3. P–T diagram for the decomposition of $NiCO_3$. o = $NiCO_3$; x = mixture of $NiCO_3$ and NiO+CO_2; Δ = NiO+CO_2.

of $(MgCO_3)_{90}(NiCO_3)_{10}$ through 20 % intervals to $(MgCO_3)_{10}(NiCO_3)_{90}$, and of $(CaCO_3)_{97}(NiCO_3)_3$ through selected intervals to $(CaCO_3)_{50}(NiCO_3)_{50}$. Lithium carbonate was added in small amounts (approximately 10 %) as a flux. The results of these runs, given in table IV, show that there is complete solid solution between $NiCO_3$ and $MgCO_3$, but very little of

$NiCO_3$ in $CaCO_3$. A 1:1 molar mixture of $CaCO_3$ and $NiCO_3$ did not yield a dolomite form.

In naturally occurring carbonates containing nickel mineral impurities, with the possible exceptions mentioned above (p. 663), there seems to be no solid solution of nickel in the carbonates. X-ray fluorescence analyses were made of ten calcites and dolomites that contained nickel mineral intergrowths, and the carbonates gave no evidence for the presence of nickel. These results are in accordance with spectrographic analyses of Goldschmidt (1954), who failed to find nickel present in carbonates containing nickel mineral intergrowths.

TABLE IV. Results of runs to determine solid solution between $NiCO_3$ and $MgCO_3$, and $NiCO_3$ and $CaCO_3$

Composition of mixture	Temp. (° C)	Pressure (kilobars)	Results
$NiCO_3$:$MgCO_3$			
9:1	450	15	SS
3:7	450	15	SS
1:1	450	15	SS
7:3	450	15	SS
1:9	450	15	SS
$CaCO_3$:$NiCO_3$			
1:1	450	15	Cn+N
8:2	450	15	Cn+N
8.5:1.5	450	15	Cn+N
9:1	450	15	Cn+N
9.3:0.7	450	15	Cn+N
9.3:0.7	550	15	Cn+N+A
9.5:0.5	450	15	Cn+N+A
9.5:0.5	550	15	Cn+N+A
9·5:0·5	450	12	Cn+tr. N
9·7:0·3	450	12	Cn

Cn = nickelian calcite; N = $NiCO_3$; A = aragonite; SS = solid solution.

The experiments treating carbonates with nickel salt solutions did not produce a solid solution of $NiCO_3$ in these minerals. It would appear that the formation of such solid solutions is not at all favoured by this type of reaction.

Hellyerite

Nickel carbonate hexahydrate (hellyerite) was first known as a synthetic compound (Rosetti-François, 1952). It was reported as a mineral species by Williams *et al.* (1959). These authors found that this compound was unstable, decomposing at room temperature to a poorly crystalline basic nickel carbonate. Williams *et al.* believe that the apparent rarity of hellyerite may in fact be due to this instability.

The structure of hellyerite has not been determined, but it may be inferred from crystal-chemical considerations and from known hexahydrated nickel compounds. The bluish colour and large negative birefringence indicate that it probably is composed of water molecules octahedrally arranged about nickel, between which lie parallel planar CO_3 groups. The formula should then be written $[Ni(H_2O)_6]CO_3$ rather than $NiCO_3.6H_2O$. This arrangement would explain the ease of decomposition of the compound as the Ni is tightly bound to the $6H_2O$ in the $[Ni(H_2O)_6]$ and weakly bound through covalent bonds to the CO_3. The behaviour of nickel in an aqueous environment will be discussed later in this paper.

Zaratite

Zaratite is found as a secondary mineral coating on nickeliferous rocks and minerals. It is usually associated with other secondary minerals, predominantly carbonates.

Data for physical and chemical properties vary significantly. The average chemical composition is close to $NiCO_3.2Ni(OH)_2.4H_2O$, but recent analyses by Williams (personal communication) give the following range: NiO, from 56·9 to 61·2 %; CO_2, from 13·5 to 15·7 %; H_2O, from 23·2 to 27·1 %. A zaratite with the composition $NiCO_3.Ni(OH)_2.3H_2O$ has been reported (Kiselev, 1938).

Synthetic and natural zaratites were studied by Fenoglio (1934) to determine the conditions of formation and the crystal symmetry. From his experimental work and some natural relationships, he came to the conclusion that zaratite was formed by the action of nickel salt solutions on hydrated magnesium carbonates, probably nesquehonite. From his X-ray data, he believed that it had cubic symmetry, with a cell edge of *a* 6·15 kX and with one formula weight per unit cell. Fenoglio's published X-ray powder patterns showed four and six rather diffuse lines. From such ambiguous data, there is no justification for the ascription of cubic symmetry to zaratite. Williams *et al.* (1959) found that their X-ray powder patterns of zaratites from Heazlewood and other localities could not be indexed on the basis of a simple cubic cell.

Due to the differences in data reported by various investigators, the question arises whether zaratite is a distinct mineral species, or is composed of more than one hydrate of nickel carbonate and perhaps Ni(OH), or a basic carbonate, which are usually (if not always) intergrown. The dehydration and crystallization of an initially basic amorphous nickel carbonate could produce a number of hydrates with different compositions.

Synthesis of zaratite. Zaratite was synthesized in several ways, one of which was a duplication of the method reported by Fenoglio (1934). The following factors suggested using other methods: zaratite is not always found with magnesium carbonate hydrates and therefore is not necessarily derived from them (in the experiments of Fenoglio, zaratite was produced from the actions of solutions of nickel salts upon the bicarbonate ion released by the dissolution of nesquehonite, not by a direct reactions of these solutions with nesquehonite); nickel salts undergo fairly rapid hydrolysis; and nickel hydroxide is found associated with zaratite and hellyerite in Tasmania.

The action of meteoric water and oxygen upon nickel sulphide minerals would form nickel sulphate complexes, which could then hydrolyse to produce some nickel hydroxide and nickel hydroxy sulphate complexes.

In the experiments of this paper, nickel hydroxide was used as a starting material and to this were added solutions in varying concentrations of nickel chloride or nickel sulphate, and either sodium carbonate or sodium bicarbonate. Freshly precipitated nickel hydroxide was allowed to stand in water saturated with CO_2, with or without the addition of sodium carbonate. These mixtures were allowed to stand at room temperature for periods up to two months. Zaratite was obtained from the mixtures involving the nickel salts, but not from the other experiments. (See table I for chemical analysis.)

Description of zaratite. X-ray diffraction patterns of six specimens of zaratite from Lancaster County, Pennsylvania, and Heazlewood, Tasmania, were poor and showed only diffuse lines. Table V gives the *d*-spacings and relative intensities for the best pattern, which was made using a Norelco Debye–Scherrer-type camera, with Mn-filtered Fe radiation. No internal standards were used and no film correction could be made because of the nature of the pattern. It could not be indexed according to cubic symmetry, and in fact appeared to be composite.

Microscopic examination showed that zaratite is composed of a mixture of nickel carbonate minerals varying from an amorphous hardened gel to fibrous microcrystalline phases. The phases were intermixed and could not be separated. Thick grains of the amorphous phase sometimes showed weak birefringence, but no interference figure could be obtained when convergent light was used. The indices of refraction varied widely, especially in the amorphous phase. The indices of refraction are given below. The fibrous types are taken together because separation was not possible; the indices are given parallel to and perpendicular to the fibres rather than in the usual manner of α, β, and γ. The indices of the amorphous phase varied from 1·585 to 1·624; parallel to the fibre, the variation was from 1·598 to 1·603; and perpendicular to the fibre, from 1·588 to 1·609. There was one fibrous phase that gave consistent optical information however, the indices of refraction being approximately α 1·597, β 1·602, and γ 1·609. The fibrous phases showed weak birefringence and undulating extinction, approximately parallel to the long axis of the fibres. No satisfactory interference figure could be obtained, but the figures seen indicate that they are biaxial. Some of the amorphous specimens were banded, and many showed conchoidal fracture patterns. Faint pleochroism was sometimes visible in the fibrous varieties. From these data, we conclude that zaratite is not a single mineral species and should not so be called.

TABLE V. X-ray diffraction data for zaratite. Fe radiation, Mn filter

2θ	d	I/I_0
12·45	8·93	s
22·00	5·07	vs
41·49	2·73	m
46·55	2·45	s
57·97	2·00	mw
60·88	1·91	w
67·47	1·74	vw
77·20	1·55	w
81·23	1·49	vw

Nickel bicarbonate

Nickel bicarbonate is a pale green compound that formed from basic nickel carbonates in a CO_2 or CO_2–H_2O atmosphere in runs of too short duration to make $NiCO_3$. It appears to be an intermediate step in the dehydration of hydrated nickel carbonates to form anhydrous nickel carbonate. Microscopic examination showed it to be composed of very fine isotropic crystals whose index of refraction was determined to be 1·668±0·002.

The X-ray diffraction pattern (table VI) gave body-centred cubic symmetry with a cell edge of a 8·383 Å; the measured density was 2·9 g/cm^3, corresponding to 5·7 $Ni(HCO_3)_2$ per unit cell; for an integral 6 $Ni(HCO_3)_2$, the calculated density is 3·06 g/cm^3.

Chemical analysis for nickel bicarbonate is given in table I.

Discussion

Of the divalent metals that form anhydrous carbonates, the free atoms of Mg and Ca have no *d*-orbital electrons while the free atoms of all others except Mn, Fe, Co, and Ni have completed (10 electron) shells. The number of electrons in the *d*-orbital shell of the transition metals increases from five to nine going from Mn^{2+} through to Cu^{2+}.

TABLE VI. X-ray diffraction data for $Ni(HCO_3)_2$. Cu-$K\alpha$, $\lambda = 1{\cdot}5405$, Ni filter

d	*hkl*	I/I_0	*d*	*hkl*	I/I_0
5·92	110	100	1·3599	611	8
3·42	211	58	1·2937	541	6
2·65	310	22	1·2643	622	9
2·42	222	19	1·2104	444	4
2·239	321	26	1·1860	710	5
2·095	400	44	1·0650	732	4
1·975	411	17	1·0485	800	4
1·875	420	12	0·9748	831	6
1·787	332	8	0·9618	662	5
1·7113	422	7	0·9373	840	6
1·6450	510	13	0·8838	930	5
1·5306	521	9	0·8553	844	6
1·4822	440	14	0·8471	941	3
1·4377	530	9	0·8067	10.2.2	1
1·3974	600	8	0·7994	10.3.1	2

Also, in the transition metal carbonates, there is a decrease in reactivity with mineral acids corresponding to an increase in the number of *d*-orbital electrons. This phenomenon can be attributed to an increase in the degree of covalency of the bonds. Goldschmidt (1954) states that with an increase in electronegativity of the metal, there is a corresponding increase in the amount of covalency towards ligands. In this case, an increase in electronegativity corresponds to an increase in the number of *d*-orbital electrons.

The relative abundance of these transition metals in the crust of the earth is in the order Fe > Mn > Ni > Cu > Co (Mason, 1958) but the order of the relative abundance of the corresponding anhydrous carbonates differs. $NiCO_3$ and $CuCO_3$ do not occur as natural minerals, but $CoCO_3$ does, and while Fe is approximately 50 times more abundant than Mn, their anhydrous carbonate minerals appear to have a closer abundance ratio. Clearly other factors than abundance must be involved in the relationships of these carbonates.

The bivalent metal carbonates form from aqueous solutions of the bicarbonate ion with metal salts. The behaviour of the transition metals mentioned above will be examined in this environment.

The metal ions are surrounded by six ligands in roughly octahedral symmetry. The greater the separation, the stronger the field. Water and CO_3 are strong field ligands, so that in both the aqueous complex and the carbonate crystals there will be a strong field. In such a field, the first six electrons will go into the d_ϵ-orbitals and will have paired spins. Additional electrons will go into the d_γ-orbitals with unpaired spins except in the case of the d^9 ion (Cu) where there will be pairing. This may be expressed diagrammatically as Co = (:) (:) (:) (.); Ni = (:) (:) (:) (.) (.); and Cu = (:) (:) (:) (:) (.). With d^7, d^8, and d^9 ions (corresponding here to Co, Ni, and Cu), the extra electrons occupy high-energy orbitals that point in the direction of the ligand. An increasing energy of activation will be required for reactions to occur as the number of d-orbital electrons increases from 5 to 9. This increase will be more marked with d^7 to d^9 ions because anti-bonding electrons in the high energy orbitals overlapping the ligands must be promoted to orbitals of still higher energy.

The degree of ligand field energy is also a function of the distortion of the orbitals, increasing with increase of distortion. Mn^{2+} undergoes no distortion (d^5 and d^{10} ions have spherical symmetry and therefore can not lead to distorted environments), while Cu^{2+} undergoes considerable distortion. The distortion for Ni^{2+} and Cu^{2+} is towards the square planar configuration. Planar complexes of d^8 ions are comparatively inert, requiring considerable electronic reorganization before reactions can occur. We can see, therefore, that of the five ions, Mn^{2+} has a minimum ligand field energy while Cu^{2+} has a large one, with Fe^{2+}, Co^{2+}, and Ni^{2+} in between. The difference between Fe^{2+} and Co^{2+} should be larger than that between Mn^{2+} and Fe^{2+} because there is a large discontinuity between the d^6 condition and the d^7.

In the present work, the author found the expected increase in the order of difficulty of synthesis of anhydrous carbonates from Mn through Fe, Co, Ni, to Cu. Experiments were conducted to precipitate the anhydrous carbonates of these metals under room conditions, and it was observed that using the same method of precipitation, good crystals of $MnCO_3$, mediocre ones of $FeCO_3$, and poor ones of $CoCO_3$ were produced during the same reaction time. No anhydrous nickel or copper carbonates were made, and even under hydrothermal conditions at temperatures up to 550° C, $CuCO_3$ was not synthesized, malachite always being the product.

It also follows that there will be a decrease of reactivity going from Mn^{2+} through to Ni^{2+} as the d-orbital shell becomes filled. Lability is a function of the degree of completeness in the filling of the shell, adding the electron contribution of the ligand to that of the cation; where the shell is completely filled, lability is low. Thus the increasing degree of inertness towards mineral acids of the transition metal carbonates going from Mn through to Ni is explained. This explanation corresponds to an increase in covalency, and is a more exact way of viewing this phenomenon.

One can see from the foregoing explanation the reason why nickel and copper do not form anhydrous carbonates as surface deposits. But $NiCO_3$ has been made at elevated temperatures, and as there are a number of possible hypothetical origins for $NiCO_3$ other than as a surface deposit, its apparent absence under these conditions must also be explained.

It might form as a contact metamorphic deposit between a basic igneous magma containing an appreciable amount of nickel either in solution or in the form of nickel sulphide minerals and a carbonate country rock. Because of the ease of thermal decomposition, a high pressure would be required to keep $NiCO_3$ from decomposing at the high temperature that would be associated with such intrusions. It is doubtful, however, whether such high pressures would be likely to occur at the depth at which such a reaction would take place. An extension of fig. 3 into the ranges involved gives estimates of the pressures that would be required for these temperatures.

Another possible condition of formation might be the invasion of a carbonate country rock by mineralizing solutions carrying nickel in the form of complex sulphate or sulphide ions. These solutions might be derived either from a basic magma or from the secondary alteration of nickel sulphide minerals. In the experiments treating carbonates with solutions of nickel salts, the anhydrous carbonate was not produced. Further, the naturally occurring carbonates containing secondary nickel minerals as inclusions did not show any nickel present in the carbonates. No solid solution occurred either in the experimental or natural conditions.

Anhydrous nickel carbonate can be produced from zaratite under relatively low temperatures and pressures in the laboratory. Under conditions of moderately shallow burial, the dehydration of zaratite might result in the formation of $NiCO_3$.

The actions of solutions of nickel salts upon nesquehonite (or other hydrated magnesium carbonates) may account for the formation of some zaratites, but field relations where magnesium carbonate hydrates are not associated with zaratite, and the experiments reported herein on the synthesis of zaratite show that the presence of magnesium carbonate hydrates is not a necessary condition for the formation of zaratite. The association of zaratite with magnesium carbonate hydrates is to be expected where both magnesium and nickel are present together in the parent rock. These hydrated carbonates probably have a very similar origin, i.e. they are secondary deposits formed from the alteration under atmospheric conditions of rocks that contain appreciable amounts of carbonate ion in association with nickel or magnesium or both. Experiments on the synthesis of magnesium carbonate hydrates show that they crystallize into distinct compounds more readily than do those of the nickel carbonate hydrates, which most probably accounts for the fact that the former form relatively well-crystallized compounds of distinct composition while the latter, at least in the case of zaratite, does not.

As hellyerite, zaratite, and nickel hydroxide are found associated with each other, a geological relationship can be established based on the chemical series, hellyerite–zaratite–nickel hydroxide. A possible reaction sequence to explain the formation of these minerals in nature is: the passage of water containing bicarbonate ion and oxygen from the air over nickel sulphide minerals forming nickel sulphates (which will be carried in solution), followed by the reaction of the nickel sulphate complexes with the bicarbonate ion (if the concentration is great enough) to form a precipitate of a hydrated nickel carbonate which, upon standing, will convert to hellyerite, or by the partial hydrolysis of the nickel sulphate complex to form nickel hydroxide; the reaction of additional solutions of carbonated water containing nickel sulphate upon nickel hydroxide would form zaratite.

The latter reactions would be likely to occur where the country rock was basic, such as the serpentinites of Tasmania and Lancaster County, Pennsylvania.

Nickel hydroxide could possibly be formed from the leaching of a nickeliferous serpentine by meteoric water, carrying away the silica and leaving the hydroxide of nickel, although the formation of a nickel hydrosilicate would be favoured under these circumstances (Rankama and Sahama, 1950).

While the mineralogical identity of zaratite is not resolved, it is probable that it is initially an amorphous basic nickel carbonate that is undergoing crystallization with loss of water, forming a number of nickel carbonate hydrates. An analogy to opal may be drawn.

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