THE AMERICAN MINERALOGIST, VOL. 50, MARCH–APRIL, 1965

DEHYDRATION OF SERPENTINE: HEAT OF REACTION AND REACTION KINETICS AT $P_{H_2O}=1$ ATM.

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ABSTRACT

Using the sensitive Herold-Planje thermocouple arrangement, 33 serpentine specimens have been examined by differential thermal analysis after identification by x-ray diffraction methods. Antigorite, chrysotile and lizardite appear to be characterized by both the decomposition temperature and the heat of dehydration. Mean characteristic temperatures for antigorite, chrysotile and lizardite are 700, 664 and 635° C. respectively, and mean ΔH values for the three polymorphs are 87.6, 98.9 and 135 cal/gm respectively. Values of ΔH correlate inversely with the temperature of dehydration and the nickel content of the serpentine. Decomposition at $P_{H_2O}=1$ atm. is described, on the average, by an order of reaction of about 0.93 and an activation energy of 95.4 Kcal/mole.

INTRODUCTION

Despite the large number of studies in which thermal techniques have been used to investigate the dehydration of serpentine, very little attention has been directed toward measuring the heat of dehydration, determining the reaction kinetics, and relating the effects of chemical composition and grain size to these variables. The few published values for the heat of decomposition are highly discordant; for example, Sabatier (1954) reported 111 cal/gm, Mchedlov-Petrosyan (1953) obtained 40.7 cal/gm, whereas Ando *et al.* (1957) found a range of values extending from 40 to 110 cal/gm. Investigations employing differential thermal analysis, many of which have been summarized by Faust and Fahey (1962), have yielded DTA peak temperatures as high as 778° C. (van Biljon 1960) while, in other cases, peak temperatures below 600° C. have been recorded. Very few studies included any attempt to control the water vapor pressure, a variable exerting considerable influence on the temperature of dehydration (Roy and Weber 1964).

Rising interest in the possible presence of serpentine on the moon (Salisbury 1960) and the subsequent use of this mineral as a source of water to supply lunar bases has prompted further investigation of the dehydration reaction for this mineral. Thirty-three serpentine samples were used to determine ΔH by triplicate analysis using the Herold-Planje differential thermocouple apparatus in a water vapor atmosphere of 15 psi.

EXPERIMENTAL

The thermocouple arrangement similar to that described by Herold and Planje (1948) consists of a platinum capsule 2.5 mm in diameter and

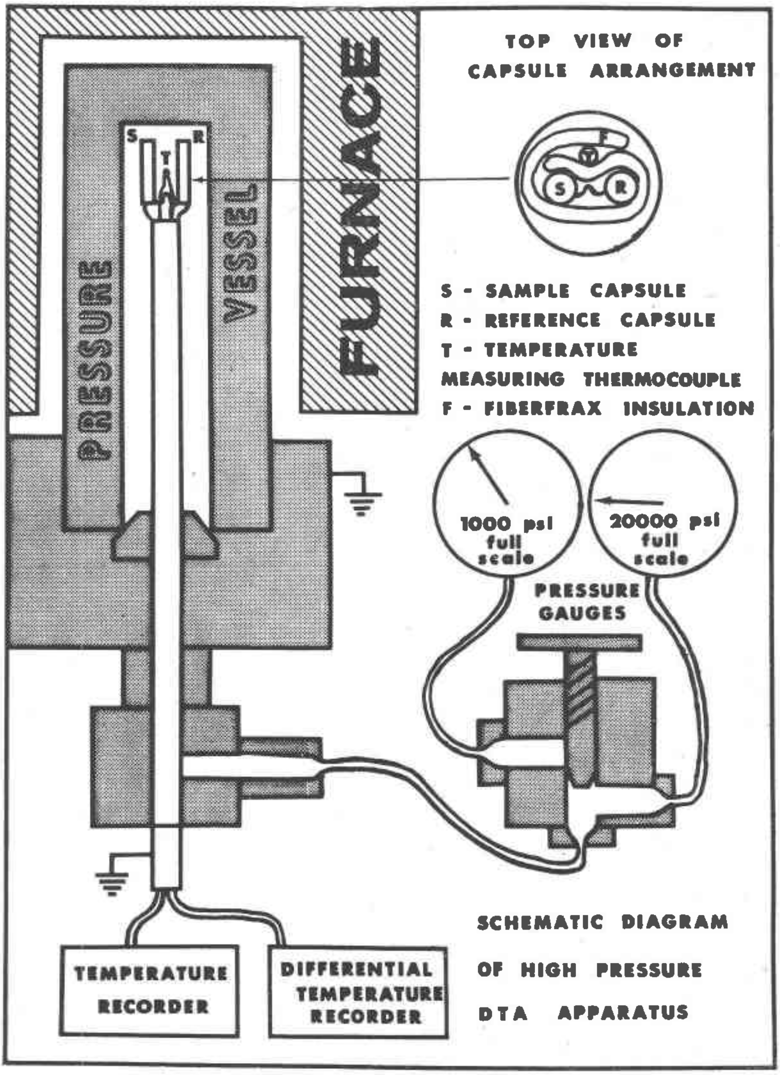

FIG. 1. Schematic diagram of differential thermal analysis apparatus designed to operate at water vapor pressures from 15 psi to 20,000 psi.

about 15 mm long, open at one end, and containing about 80 mg of sample (Fig. 1). A sealed capsule of similar dimensions, filled with Al_2O_3, serves as the "reference standard." The capsules are connected by a wire of Platinel thermocouple alloy (Accinno and Schneider 1960) welded to the capsule walls. In this arrangement, the capsules themselves serve as the thermocouples. Theoretical analysis of the heat transfer by Sewell

(1952, 1955) has demonstrated that the area under the DTA peak is proportional to the heat of reaction per unit mass of reacting material, and that the peak area is independent of the heating rate provided it is linear, the rate at which the reaction takes place, and the specific heat of the sample. To a first approximation, the peak area is also independent of the thermal conductivity of the sample.

The thermocouple arrangement shown in Fig. 1 is mounted in a 2″ O.D. stellite pressure vessel in which water pressures from 15 psi to 20,000 psi can be generated and measured. The noble metal Platinel thermocouple alloys provide an emf similar to that of chromel-alumel, and the voltage from the differential couple is amplified with a solid-state d.c. Acromag amplifier with a noise level of 1 microvolt and drift of about 5 microvolts.

ΔH measurements were obtained from the area under the DTA curve using a calibration curve constructed from peak areas obtained by fusion and/or inversion of a variety of compounds with known heats of reaction. The heating rate, about 10° C./min, was shown to the linear over the temperature range in which serpentine decomposed.

The value of kinetic data obtained from differential thermal analysis is limited by three factors:

> (1) the temperature is changing while the reaction is taking place, whereas ideally, isothermal dehydration methods such as weight loss technique provide more reliable and precise kinetic data, and in addition, provide some information concerning the reaction mechanisms. (2) The concentrations of the reactant and products at any given time are determined indirectly by temperature difference (between a sample and the reference standard) resulting from heat transfer during the reaction. Since heat transfer is not instantaneous, precise determination of concentrations is not possible. (3) It is necessary to assume that an equation relating the rate of change in concentration of the reactant to the concentration of the remaining reactant is a reasonable description of reality, and such factors as the shape of the reactant particles are not taken into account.

Some of the difficulties have been evaluated and are discussed by Borchardt (1957), and Borchardt and Daniels (1957). Among the most important assumptions inherent in the determination of rate constants from DTA are:

> (1) the temperature of the reactant is uniform, (2) the area under any appreciable portion of the DTA curve is proportional to the heat absorbed during the time interval in which that portion of the DTA curve was recorded, and this quantity of heat is in turn proportional to the mass of the sample which reacted during this time, (3) the kinetics of the reaction can be described by a single rate constant, and (4) the activation energy does not vary with temperature during the reaction.

The strongest support for the value of kinetic data derived from differential thermal analysis was provided by Tsuzuki and Nagasawa (1957). These authors obtained weight loss curves and DTA curves from the same samples. Kinetic parameters calculated from weight loss data were used to construct theoretical DTA curves for comparison with DTA curves obtained by actual experiment. They conclude that the DTA curve faithfully follows the change in decomposition rate, except for a slight difference in peak temperatures.

Assuming a relationship between the rate of reaction and the concentration of remaining reactant: $-dc/dt = k\ c^n$, where dc/dt is the change in concentration of reactant with time t, c is the concentration of the unreacted sample, k is the rate constant and n is the order of reaction, k can be determined if n is known, and if measurements of dc/dt and c are available. The latter can be obtained from relative areas under the DTA curve. Using the Arrhenius equation, $k = A\ e^{-E/RT}$, where E is the energy of activation, A is a constant, R is the gas constant and T is the absolute temperature, it is possible to determine both k and n by a digital computer program which calculates a set of k values for each set of dc/dt and c measurements, using an arbitrary value for n. The value of n which provides the best fit of the concentration data to the Arrhenius equation is taken as the observed order of reaction. In practice, up to 20 measurements of dc/dt, c, and T[1] are taken from each DTA curve, and 21 sets of log k vs 1/T values are computed for values of n ranging from zero to 4.0, in 0.2 increments. Linear regression lines are automatically drawn for each set of log k vs 1/T values, correlation coefficients are computed, and the most linear plot is the criterion used in selecting n. The activation energy is computed from the Arrhenius equation.

Quantitative spectrochemical analyses were made for Fe, Mn, Ni, Ti and Cr using cobalt as an internal standard. Details of the method are described by Joensuu and Suhr (1962). Ferrous iron was determined by $KMnO_4$ titration (R. T. Greer, analyst). Specimens were identified by *x*-ray diffraction using the method of Whittaker and Zussman (1956).

DISCUSSION OF EXPERIMENTAL VARIABLES

Water Vapor Pressure. The effect of P_{H_2O} on the metastable dehydration temperature of kaolinite was demonstrated by Stone (1954) and by Ellis and Mortland (1961) who showed that dehydration temperatures increase with increasing water pressure. Using the apparatus described above, Roy and Weber (1964) determined the p-T curve for the decomposition of serpentine at water pressures extending from 15 psi to over 10,000 psi, and found that the temperature of dehydration increased with increasing P_{H_2O} up to about 7000 psi, above which the stable de-

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[1] The temperature of the sample. This is obtained by subtracting the temperature difference between the sample and reference capsules (determined from the height of the DTA curve above the base line) from the temperature indicated by the recording thermocouple.

hydration reaction was encountered (Roy and Osborn 1954). For the measurements of ΔH in this study, P_{H_2O} was held constant at 15 psi.

Particle Size. A number of authors have demonstrated a relationship between the DTA temperature of dehydration and the particle size of serpentine samples; recent studies include Martinez (1961), Veniale (1962) and Hoyos and Delgado (1961). Although very fine particles will dehydrate at somewhat lower temperatures than material with coarser micelle size, it appears that the effect of particle size as such has been somewhat overemphasized. Bayliss (1964) carefully prepared size fractions of high-purity calcite by repeated gentle tapping and sieving, an attempt to comminute by separation along cleavage planes without generating appreciable structural damage. DTA curves obtained from the dissociation of $CaCO_3$ in a controlled atmosphere of CO_2, and with a heating rate of 15° C./min, were identical. Size fractions as coarse as 35 to 48 mesh indicated the same dissociation temperature as samples whose particles ranged in size between 1.6 and 1.16 microns. Variations in the temperature of dissociation are attributed by Bayliss to variations in the degree of structural damage produced in the grinding process. Roy and Weber (1964) determined the dehydration temperature of serpentine as a function of pressure for two size fractions prepared by repeated percussion crushing and sieving: 80–100 mesh and −325 mesh. An analysis of covariance performed with these data shows no clear evidence of a particle size effect. In this case, some of the structural damage produced on grinding may have been annealed at high water pressures before dehydration was effected.

Brindley and Hayami (1964) discuss kinetics of dehydration in relation to particle size.

Samples of massive serpentine used in this study were reduced to −325 mesh by repeated percussion crushing and sieving. Fibrous varieties were emplaced in the platinum capsules without any attempt at size reduction.

Sample Purity. Since peak areas are associated with a measured weight of sample to determine the heat of reaction, the presence of impurities will cause erroneous, low values of ΔH. An impurity amounting to 1% will inject an error of about 1% in ΔH determinations. Serpentine minerals are seldom found in experimentally useful quantities without associated minerals such as magnetite, chromite, etc. Serpentine derived from the alteration of ultrabasic rocks, for example, will contain inclusions of iron oxide minerals since relatively little iron of the original olivine enters the serpentine structure. Samples used in this study were broken into +20 mesh fragments and hand-picked under the binocular microscope. A small quantity of the selected material was examined by *x*-ray diffraction, several milligrams were used for spectrochemical analysis and the remainder was consumed by chemical analysis for Fe^{2+} and by differential thermal analysis.

Errors Associated with Differential Thermal Analysis. Small variations in packing of the sample, position of the thermocouples in the furnace, heating rate linearity, and experimental errors involved in measuring temperature and areas under the DTA curve were evaluated by replicate analysis of several samples. The observed standard deviations for measurement of the characteristic temperature[2] and heat of reaction are 2° C. and 8 cal/gm respectively. Construction of the base line introduced the greatest source of error in ΔH determinations; for certain specimens with sharp DTA peaks, the standard deviation of ΔH determination was as low as 1.9 cal/gm. All samples were examined by DTA in triplicate.

RESULTS AND DISCUSSION

Heats of Reaction. Dehydration data are presented in Table 1. Considerable variation in characteristic temperature, T_c, and in ΔH are apparent from sample to sample for the serpentines as a whole. For other minerals studied, for example kaolinite, differences in ΔH among samples from various localities were very small. Since, in the case of serpentine, these variations are greater than can be accounted for by experimental error and sample impurity, they are considered to be real. Summary statistics are provided in Table 2. When the samples characterized as more or less pure polymorphs (as opposed to mixtures of chrysotile, lizardite, and antigorite) are examined, it is found that the antigorites, chrysotiles and lizardites exhibit different mean characteristic dehydration temperatures (700, 664 and 635° C. for antigorite, chrysotile and lizardite respectively). The heat of dehydration also appears to be related to the variety of serpentine; mean values of ΔH are 87.6, 98.9 and 135 cal/gm for antigorite, chrysotile and lizardite respectively.

Multiple correlation analysis (Table 3) revealed a number of relationships between the decomposition temperature, the heat of reaction, and the chemical composition (spectrochemical analyses are reported in Table 4). At the one per cent level of significance, a striking inverse

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[2] Defined as the temperature at the point where the tangent to the maximum slope of the DTA curve intersects the base line. This temperature is more reproducible than peak temperature and is considered to be the best measure of the temperature at which reaction begins; the DTA apparatus was calibrated using *characteristic* temperatures of a variety of well characterized chemical compounds.

TABLE 1. DEHYDRATION DATA FOR SERPENTINES CRUSHED TO −325 MESH (EXCEPT FIBROUS VARIETIES). $P_{H_2O} = 1$ ATM.

Serial Number	Description[1]	ΔH cal/gm	Characteristic temperature ° C.[2]	Peak temperature ° C.	Observed order of reaction n	Activation energy, E KCal/mole
1	SM-13079. Brilliant yellow-green. Syracuse, New York. Mixture of antigorite and lizardite.	104	653	704	1.5	126
2	AMNH-13757. Brilliant yellow-green. Snarum, Norway. Mixture of lizardite and chrysotile.	96.1	639	694	0.7	83.1
3	AMNH-17501. Light green. Broughton, Ontario. Chiefly chrysotile.	116	663	708	0.5	103
4	P-B5292. Medium green-gray. Cedar Hill quarry, Lancaster Co., Pennsylvania. Antigorite.	90.0	701	735	2.0	150
5	SM-R10581. Medium green. Argent Tunnel, Tasmania. Chiefly lizardite.	157	636	700	1.0	86.6
6	AMNH-13803. Medium green-gray, platy. Val Antigorio, Novara Province, Piedmont, Italy. Antigorite.	101	689	725	1.5	174
7	ROM-M21454. Dark green. Rennie twp., Sudbury District, Ontario. Chiefly lizardite.	121	640	702	1.0	87.4
8	ROM-M25510. Medium green-gray. Bournon Pit, Deloro Twp., Ontario. Antigorite and lizardite.	121	666	714	0.8	103
9	AMNH-29597. White. Wakefield, Quebec. Chrysotile and lizardite.	169	622	686	0.8	53.7
10	SM-105834. White. Kilmar, Quebec. Chiefly lizardite, probably some chrysotile.	95.6	619	679	0.5	59.8
11	ROM-M6432. Light yellow. Templeton, Ottawa Co., Quebec. Lizardite.	121	631	690	0.4	63.4
12	SM-93776. White. Hsiu-yen Hsien, Liaoning Province, Manchuria. Antigorite.	77.8	708	758	1.0	120
13	SM-116827. Brilliant sea-green. Texas, Lancaster Co., Pennsylvania. Antigorite.	78.9	713	766	2.2	127

[1] AMNH—American Museum of Natural History.
P—Pennsylvania State University.
ROM—Royal Ontario Museum.
SM—Smithsonian Institution.

[2] Considered to be the temperature at which the dehydration reaction begins (see text).

TABLE 1—(*continued*)

Serial Number	Description[1]	ΔH cal/gm	Characteristic temperature ° C.[2]	Peak temperature ° C.	Observed order of reaction n	Activation energy, E KCal/mole
14	SM-47656. Light yellow-white. Gordon's quarry, near Montville, Morris Co., New Jersey. Chrysotile and lizardite.	81.4	647	704	0.8	73.9
15	ROM-E2950. Medium green-gray. Piedmont, Italy. Mixture of antigorite and lizardite.	108	642	705	1.0	77.0
16	ROM-M13855. Light yellow. MacDonnell Ranges, Australia.	141	634	693	0.2	68.4
17	ROM-M22245. Light yellow. Wakefield, Quebec. Mixture of chrysotile and lizardite.	123	643	692	0.2	61.3
18	ROM-M19410. Light yellow. Kilmar, Quebec. Mixture of chrysotile and lizardite.	125	627	689	0.2	71.1
19	P-B5296. Dark green. Eden Mills, Vermont. Mixture of antigorite and lizardite.	89.0	636	716	1.5	67.0
20	P-B5294. Light green-gray. Asbestos, Quebec. Chrysotile with some lizardite.	97.3	663	712	0.8	112
21	P-B5281. Light yellow-green. Cornwall, Pennsylvania. Chrysotile with some antigorite.	129	640	696	0.5	74.0
22	ROM-M16255. Light green, long fiber. A-Nil Desparandum, Shabani, Southern Rhodesia. Chrysotile.	97.6	663	719	1.5	112
23	ROM-M16254. Dark green. A-Nil Desparandum, Shabani, Southern Rhodesia. Chiefly antigorite.	79.3	694	748	1.3	106
24	P-B5289. Long fiber, yellow. Globe, Arizona. Chrysotile.	99.8	662	702	0.2	87.5
25	P-B5291. Light green. Cedar Hill quarry, Lancaster Co., Pennsylvania. Mixture of antigorite and chrysotile.	108	675	737	2.2	114
26	ROM-M23011. Med. green, medium length fiber. Bazhenovo, Urals, U.S.S.R. Chrysotile.	82.8	667	719	0.6	77.4
27	ROM-M17371. Light green-yellow, long fiber. Deloro Twp., Ontario. Mixture of chrysotile and lizardite.	95.1	652	700	0.6	69.9
28	ROM-M13855. Yellow, medium length fiber. MacDonnell Ranges, Australia. Chrysotile.	81.5	664	707	1.0	107

TABLE 1—(*continued*)

Serial Number	Description[1]	ΔH cal/gm	Characteristic temperature ° C.[2]	Peak temperature ° C.	Observed order of reaction n	Activation energy, E KCal/mole
29	ROM-M6432. Light yellow, long fiber. Templeton, Ottawa Co., Quebec. Chrysotile.	119	666	705	0.3	80.2
30	P-B5298. Dark green. Styria, Austria. Antigorite.	98.8	698	732	2.0	154
31	P-LV12. Light green, long fiber. Thetford Mines, Quebec. Chrysotile.	88.2	675	712	0.2	89.8
32	ROM-M19410. Short fiber, yellow. Kilmar, Quebec. Chrysotile.	102	660	702	0.2	69.9
33	ROM-E3081. Light yellow-orange, long fiber. Grand Canyon, Arizona. Chrysotile.	103	668	711	1.6	138

TABLE 2. SUMMARY STATISTICS FOR THE DEHYDRATION OF SERPENTINE

	No. of Specimens	Characteristic temperature ° C.		ΔH cal/gm		Ni content ppm	
		Mean	s.d.	Mean	s.d.	Mean	s.d.
Serpentines, chiefly fibrous	12	670	13.5	96.3	11.7	790	838
Serpentines, chiefly massive	21	653	27.9	112	24.6	513	1000
All serpentines	33	659	24.9	106	21.9	613	942
High nickel serpentines (Av. 1500 ppm)	13	675	23.7	101	21.6		
Low nickel serpentines (below 100 ppm Ni)	18	649	21.4	110	22.8		
Antigorites	6	700	8.87	87.6	10.5		
Chrysotiles	9	664	2.55	98.9	13.2		
Lizardites	4	635	3.78	135	17.4		

TABLE 3. MATRIX OF CORRELATION COEFFICIENTS

	T_c	T_p	n	E	Total Fe	FeO	Mn	Cr	Ni	Ti
ΔH	−.59	−.57	−.31	−.38	−.17	−.22	−.07	.12	−.28	−.04
T_c		.91	.57	.78	.26	.38	−.05	.21	.65	−.22
T_p			.70	.67	.25	.34	−.08	.22	.75	−.00
n				.73	.28	.29	.14	.21	.69	.14
E					.31	.39	.16	.30	.51	−.20
total Fe						.70	.08	.33	.31	.11
FeO							.20	.39	.28	−.01
Mn								−.16	−.24	.08
Cr									.37	−.08
Ni										−.01

T_c = characteristic temperature.

T_p = peak temperature.

Values of r greater than .449 and .349 are significant at the 1% and 5% levels respectively.

correlation is substantiated for ΔH and T_c, that is, samples which decompose at higher temperatures tend to have a lower heat of reaction. Chromium, titanium and manganese are not correlated with ΔH or T_c, but a positive correlation of nickel and iron with T_c, and a negative correlation of these elements with ΔH are evident.

Although not all of the variation in ΔH is statistically accounted for by these relationships, the 13 high nickel serpentines (average 1500 ppm Ni) exhibit a much higher characteristic temperature of dehydration (675° C.) than the group of 18 serpentines whose nickel content is below 100 ppm ($T_c = 649°$ C.). The mean ΔH for the high nickel category (101 cal/gm) is lower than the average heat of reaction for the low nickel group (110 cal/gm) and evidence that this difference is real is provided by a Student-t test of means at the one per cent level of significance. The variation of ΔH with T_c is demonstrated more clearly by considering the high nickel serpentines as a separate group: this relationship is illustrated in Fig. 2 where ΔH is plotted against the temperature of dehydration for the massive serpentines containing 1000 ppm or more of nickel. Serpentine samples with lower nickel contents are situated below this curve and show a less distinct but statistically substantiated relationship between ΔH and T_c.

These observations may be explained, at least in part, by an evaluation of factors which influence the stability of the serpentine structure.

Detailed understanding of these factors in the study of naturally occurring samples has been considerably hampered by the difficulty of obtaining measurable quantities of a large number of specimens of the pure material for both structural and chemical analysis.

The stability of serpentine is influenced largely by the degree of mismatch between the octahedral brucite layer and the adjacent tetrahedral Si-O sheet, imperfect matching resulting from the different dimensions of the two layers. Better matching of the octahedral and tetrahedral layers can be achieved by the formation of a tubular structure with the

TABLE 4. CHEMICAL COMPOSITION

Serial Number	Total Iron Fe%	FeO%	Mn ppm	Cr ppm	Ni ppm	Ti ppm
1	1.6	0.20	230	<100	<100	130
2	1.3	0.58	50	<100	<100	100
3	1.8	0.50	220	<100	350	<100
4	0.94	0.63	250	550	1400	<100
5	1.5	0.23	100	2400	1000	<100
6	4.7	3.03	620	1400	1400	160
7	2.4	0.70	130	800	740	330
8	2.5	0.19	160	<100	1150	940
9	<0.1	0.15	180	<100	<100	170
10	0.13	0.24	77	<100	<100	120
11	0.39	0.22	500	<100	<100	340
12	1.25	1.18	300	<100	<100	<100
13	0.40	0.58	40	240	4300	<100
14	0.29	0.13	660	<100	<100	120
15	4.9	4.28	1000	<100	<100	340
16	0.42	0.27	150	<100	<100	<100
17	<0.1	0.14	540	<100	<100	220
18	0.20	0.01	700	<100	<100	<100
19	2.2	0.65	500	140	440	2100
20	1.7	0.89	150	<100	<100	<100
21	1.7	0.50	210	<100	<100	<100
22	0.82	0.16	100	<100	1150	100
23	3.4	1.70	80	1300	2000	130
24	0.45	0.29	85	<100	<100	<100
25	2.7	1.43	320	150	1900	160
26	1.2	0.41	280	<100	980	200
27	6.9	0.23	340	<100	720	<100
28	0.26	0.16	550	<100	<100	<100
29	0.20	0.17	180	<100	<100	<100
30	5.8	4.09	480	630	2100	<100
31	3.2	3.49	190	1400	630	<100
32	0.1	0.12	320	<100	<100	<100
33	0.34	0.13	1600	<100	<100	<100

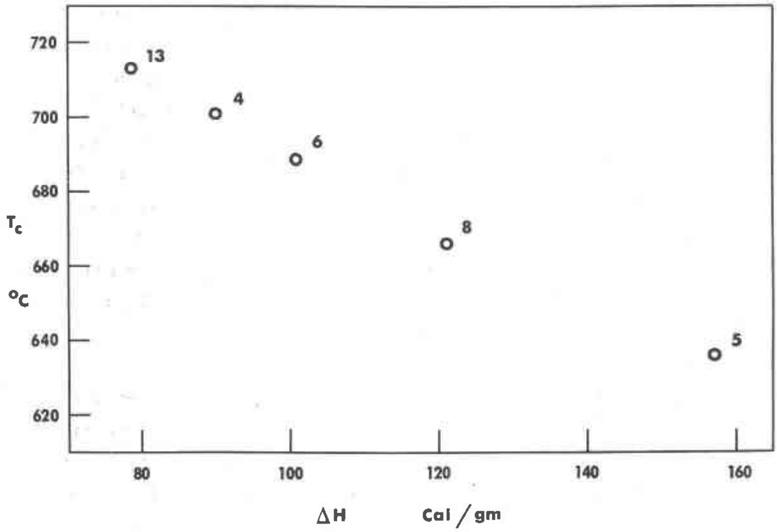

FIG. 2. Relationship between the "characteristic" dehydration temperature and the heat of reaction for the massive serpentines containing 1000 or more ppm of nickel.

brucite layer on the convex side of the curve (chrysotile), by isomorphous substitution of cations providing stronger interlayer bonds, and by isomorphous substitution of larger cations for Si or smaller cations for Mg providing a corrugated or platy structure (antigorite and lizardite). A number of chemical analyses, considered to be highly reliable, have been collected by Deer *et al.* (1962), Faust and Fahey (1962) and Bates (1959). After calculation of the number of ions on the basis of 9(O, OH), several relationships emerge above the errors inherent in chemical and structural analysis:

(1) the sum of the tetrahedral cations (Si, Al, Fe^{3+}) for samples classified as chrysotile and lizardite is somewhat below the ideal value of 2, and the number of OH ions is greater than the value of 4 required by the ideal formula of serpentine, (2) for samples classified as antigorites, Σ octahedral, Σ tetrahedral, and Σ OH are much closer to the stoichiometric values, (3) Al is often more abundant in antigorite than in chrysotile and lizardite, although striking exceptions are found, (4) in chemical analyses, Ni is more often reported in antigorites although exceptions are known, (5) nickel rich serpentines usually contain less (OH) than specimens with lower nickel contents, (6) for many chrysotile analyses there are more (OH) ions than the number required to balance (by substitution for O in the Si-O tetrahedra) the charge deficiency caused by substitution of Al and Fe^{3+} for Si.

Several reliable analyses are remarkably anomalous, for example, the chemical composition of the serpentine from the Shetland Islands reported by Brindley and von Knorring (1954). McConnell (1954) suggested that the excess (OH) ions were present in the tetrahedral layer and demonstrated that the analysis of Brindley and von Knorring could be recast in a formula different by less than 1% from the stoichiometric formula by including (H_4) in the Si-O layer. On the basis of 4(OH), the sum of Si (1.75), Al (0.01) and H_4 (0.24) is 2.00, and the charges are balanced. It appears that for the chrysotiles and the lizardites, tetrahedral cation deficiencies possibly caused by insufficient Si cations, are balanced by appreciable substitution of OH ions. As Bates (1959) points out, this arrangement would weaken the structure and require a tubular or corrugated habit. The stability of this polymorph would be slightly lower than serpentine with a greater ratio of tetrahedral to octahedral cations, which requires none or less (OH) substitution and which would exhibit a platy habit.

The effect of nickel substitution for magnesium on the stability of serpentine was demonstrated with synthetic materials prepared by Roy and Roy (1954). The upper stability temperature reported by these authors for Ni-Si serpentine is 530° C., compared to 490° C. for Mg-Si serpentine. Presumably, this arises from the greater interlayer bond strength resulting from the greater percentage of covalency in Ni-O bonds than in Mg-O bonds.

A review of a large number of thermal analyses of serpentine by Faust and Fahey (1962) indicates that serpentines which can be called antigorite dehydrate at higher temperatures than the tubular and corrugated varieties. DTA peak temperatures for antigorite are generally above 750° C., whereas endothermic peaks for specimens of chrysotile and lizardite appear between 680 and 750° C. The data in Table 2 suggest that all three polymorphs are characterized by distinctly different dehydration temperatures and heats of dehydration, indicating that DTA may be used in conjunction with complex x-ray methods in the classification of serpentine.

In summary, serpentine with a tubular or corrugated structure appears to be characterized by higher (OH) content and lower stability compared to platy varieties, and increasing concentration of nickel, by increasing the strength of interlayer bonding, raises the upper limit of stability. These observations are consistent with the relationships between ΔH, T_c and the nickel content reported here. Other variables, however, must also affect the heat of reaction. It would be expected that specimens with higher ferrous iron content would exhibit lower values of ΔH, since oxidation of the iron during dehydration is an exothermic reaction and the effects would be superimposed upon the endothermic dehydration effect. The difficulty of determining how much of the Fe^{++} reported in chemical analyses is actually in the structure rather than present as minute inclusions of iron oxides makes evaluation of this variable difficult.

Kinetic Data. The mean value for the order of reaction, n, is 0.93 but the standard deviation of 0.62 indicates considerable variation from sample to sample. The activation energy (average 95.4 Kcal/mol; standard deviation 30.1) exhibits similar variation. Triplicate analysis shows that these differences are characteristic of the sample and are not caused by experimental error. Such large variations are not observed for other minerals studied with the same apparatus. The matrix of correlation coefficients of Table 3 shows that the activation energy is negatively correlated with ΔH, and positively correlated with the dehydration temperature ($r=0.78$), the ferrous iron content, the concentration of nickel, and the order of reaction. Higher orders of reaction for the nickel rich serpentines would indicate that at equivalent stages of the reaction (i.e. concentration of remaining reactant) the structure of the weaker low nickel varieties is decomposing at a greater rate than the structure of the high nickel serpentines. Lizardites exhibit the lowest activation energy (mean 76.4 Kcal, s.d. 12.4) and antigorites the highest (mean 138 Kcal, s.d. 25.2); chrysotiles are intermediate (mean 96.1 Kcal, s.d. 21.1).

ACKNOWLEDGMENT

We are indebted to Professor Rustum Roy, in whose laboratories this investigation was made, for discussion and review of the manuscript, to Dr. Brian Mason, Dr. J. A. Mandarino, Dr. D. C. Harris and Dr. D. E. Desautels for subsamples of museum specimens, and to N. Suhr for supervision of the spectrochemical analyses. Research reported in this paper was sponsored by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under contract No. AF 19(628)-2773.

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Manuscript received, July 29, 1964; accepted for publication, January 26, 1965.