

Geologic Thermometry*

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ABSTRACT

The methods of measuring and estimating temperatures of geologic processes are examined critically. Data for some of the more accurate methods of wide geologic application are summarized by means of tables and graphs. Attention is called especially to two methods that have been used increasingly the last several years: (1) study of liquid inclusions and (2) determination of fractionation of stable isotopes.

INTRODUCTION

Increase of interest in geologic thermometry has been marked during the past 25 years. Numerous summaries and reviews have appeared, both of the entire field (Seifert, 1930; Bowen, 1928; 1940a) and of certain aspects of the subject, such as the temperature of magmas (Larsen, 1929), hydrothermal synthesis of minerals (Morey and Ingerson, 1937), inclusion thermometry (Smith, 1953), and phase-equilibrium relations in silicate melts (Eitel, 1954).

The present paper is intended to summarize the data of geological significance, largely in tabular and graphic form, and to give brief evaluations of the usefulness and accuracy of each method discussed. For details of techniques the original references must be consulted. A more complete review is in preparation (Ingerson, in press).

ACKNOWLEDGMENTS

The subject of geologic thermometry is developing at such a rate that many of the most interesting and important results thus far obtained have not yet appeared in print. Several research workers have very generously made their results available for this symposium in advance of publication. It is a pleasure to record here with much appreciation such assistance from Joseph Berman, U. S. Bureau of Mines; A. F. Buddington, Princeton University; C. Emiliani, Institute for Nuclear Research, University of Chicago; H. P. Eugster, Geophysical Laboratory of the Carnegie Institution; J. J. Fahey, U. S. Geological Survey; Julian Goldsmith, University of Chicago; Donald Graf, Illinois State Geological Survey; Angelina Vlisidis, U. S. Geological Survey; and H. S. Yoder, Geophysical Laboratory of the Carnegie Institution. Specific credit is given in each table or figure where previously unpublished data are cited.

DIRECT MEASUREMENT OF TEMPERATURES

Where temperatures can be measured directly by thermometer or thermocouple, accuracy is very high, commonly within 1°C if calibration is good. Measurements of temperatures of inaccessible lava flows or fountains with optical pyrometers may be too low by 20°C or more.

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Temperatures as high as 645°C in fumaroles have been measured (Zies, 1929, p. 8).

Basaltic lava at vents commonly is between 1050° and 1150°C. Temperatures of 1200°–1300°C are occasionally produced locally by exothermic gas reactions. Such lavas become immobile at 700°–780°C (Macdonald, 1954, p. 175).

Siliceous lavas are usually so explosive that their extrusion temperatures cannot be measured. Washington estimated that a dacitic lava on Santorin was extruded between 800° and 900°C (Bowen, 1928).

EXPERIMENTAL MELTING OF ROCKS

Minakami (1951) found that basalt had to be heated 100°C hotter in the laboratory to reproduce the viscosity it had at a given temperature in nature. The difference is probably much greater for dry melts of more siliceous rocks, because of their higher content of water in nature.

Goranson (1931; 1932) melted granite under a pressure of 1000 atmospheres of water vapor at 700°C. This temperature accords much better with field evidence on the intrusion temperature of granite than does its dry "melting point" of around 1050°C.

INDIRECT METHODS

Many indirect methods have been used in estimating temperatures of geologic processes. Some of these give only maxima or minima and must be used with other methods to establish a temperature range. Under favorable circumstances other methods can give results that approach direct measurement in accuracy.

MELTING POINTS

Melting points of minerals indicate maximum temperatures above which the respective minerals cannot have formed. These melting points are not very useful in determining actual temperatures of formation because the minerals may crystallize a few degrees below their melting points (low-melting sulfides) or many hundreds of degrees below (high-melting silicates or oxides formed hydrothermally at low temperatures). For a list of melting points of minerals *see* Kracek (1942).

TRANSFORMATION TEMPERATURES

Many minerals can exist in two or more crystalline modifications. Forms that show irreversible transformation are said to be *monotropic*; reversible, *enantiotropic*.

Monotropic pairs.—When one mineral transforms irreversibly to another of the same composition the first is unstable with respect to the other at all temperatures. When such a metastable phase forms at low temperatures the rate of transformation may be very slow, and the unstable form can remain for considerable time.

There is no definite temperature at which a monotropic transformation takes place; the rate depends on the temperature, pressure, and other factors. Marcasite, for example, changes to pyrite at an appreciable rate at 450°C, and aragonite goes rapidly to calcite at about 400°C. Marcasite can be prepared in the laboratory below 300°C by the action of H₂S on ferric sulfate or chloride. The best temperature range for the formation of aragonite appears to be 30°–70°C, but much of it is no doubt formed in nature outside and especially below this range. Formation of aragonite is

favored by the presence of small amounts of Ba, Sr, Mg, Pb, or CaSO₄ in the solution from which the aragonite crystallizes.

Anatase and brookite are both monotropic with respect to rutile. The former goes to rutile at an appreciable rate around 400°C in the presence of a flux; the latter below 800°C.

Enantiotropic relations.—Reversible transformations take place at a definite temperature (with constant composition and under a given pressure), called the *inversion point*. If a mineral has only two forms and the inversion point is high (*e.g.*, nephelite-carnegieite, 1248°C) it has little or no more meaning in geologic thermometry than does a melting point. On the other hand, minerals with inversion points within the range of geologically interesting temperatures can be very useful. This is especially true of compounds with two or more inversion points.

Caution must be used in the interpretation of inversion points, not only in determining which phase was the original modification, but also whether it was a stable or metastable form. For example, tridymite or cristobalite can form as a metastable phase at temperatures where low quartz is the stable form of silica and, if cooled rapidly, persist over considerable periods. Larsen and others (1936, p. 694) point out that these minerals are unknown in pre-Tertiary rocks.

The effects of composition and pressure must also be considered. Inversion temperature in a solid-solution series varies with composition. (*See* clinoenstatite, Table 1.) Even in minerals in which no solid solution is known, such as quartz, impurities taken up at higher crystallization temperatures can lower the inversion point (Keith and Tuttle, 1952).

TABLE 1.—*Inversion points of minerals*

Mineral	Composition	Inverts to	T (° C)	Remarks*
Cryolite	Na ₃ AlF ₆ (monoclinic)	Cubic form	560	
Low quartz	SiO ₂	High quartz	573	
High quartz	SiO ₂	Tridymite	870	
Tridymite	SiO ₂	Cristobalite	1470	
Microcline	KAlSi ₃ O ₈ (triclinic)	Sanidine (monoclinic)	700±	Laves (1952, p. 447).
Microcline	KAlSi ₃ O ₈	Sanidine	525 (hydrothermal)	
Albite	NaAlSi ₃ O ₈	α-β ("analbite")	700	Bowen and Tuttle (1950, p. 501).
Anorthite	CaAl ₂ Si ₂ O ₈	X-ray (c-) reflections become increasingly diffuse to m.p.	1100±	Laves and Goldsmith (1954).
Enstatite	MgSiO ₃ (orthorhombic)	Clinoenstatite	1140	Bowen and Schairer (1935, p. 217).
Enstatite	90% FeSiO ₃ 10% MgSiO ₃	Clinoenstatite	955	Bowen and Schairer (1935, p. 217).

* All data are from Kracek (1942) unless otherwise noted.

The effect of pressure on inversion can be calculated by use of the Clausius-Clapeyron equation. Calculation and experiment agree that 1000 atmospheres pressure raises the inversion temperature of low quartz about 20°C (Gibson, 1928).

Some inversion points of minerals are given in Table 1. For a more extensive list see Kracek (1942).

DISSOCIATION AND DECOMPOSITION

Dissociation and decomposition temperatures of minerals (including incongruent melting temperatures), like melting points, commonly give only maximum temperatures above which the respective minerals cannot have formed. A mineral containing a volatile component such as CO₂ or H₂O, however, can form under high pressures at temperatures above those at which it will dissociate at lower pressures.

The possibility of reactions with other components must be kept in mind when making interpretations involving dissociation or decomposition. Calcite, for example, will react with silica at atmospheric pressure almost 400°C below the temperature at which calcite alone begins to dissociate.

Table 2 gives some dissociation and decomposition temperatures of geologic inter

TABLE 2.—*Dissociation and decomposition temperatures of minerals*

Mineral	Composition	T (° C)	Products	Remarks*
Pyrite	FeS ₂	dissoc. 690 (1 atm. S)	FeS _x + S
Calcite	CaCO ₃	dissoc. 885 (1 atm. CO ₂)	CaO + CO ₂
Dolomite	CaMg(CO ₃) ₂	500 (1 atm. CO ₂)	MgO + CO ₂ + CaCO ₃
		890	CaO + CO ₂ + MgO	
Magnesite	MgCO ₃	dissoc. 373 (1 atm. CO ₂)	MgO + CO ₂
Siderite	FeCO ₃	dissoc. 282 (1 atm. CO ₂)	
Malachite	CuCO ₃ ·Cu(OH) ₂	decomp. 200	
Anthophyllite	Mg ₇ (Si ₈ O ₂₂)(OH) ₂	decomp. 900	MgSiO ₃ + SiO ₂	Thilo and Rogge (1939, p. 346).
Danburite	CaO·B ₂ O ₃ ·2SiO ₂	decomp. 1000±	2 liquids	Morey and Ingerson (1937, p. 46).
Serpentine	Mg ₆ Si ₄ O ₁₁ (OH) ₆ ·H ₂ O	500	forsterite + talc	Bowen and Tuttle (1949, p. 447).
Talc	H ₂ Mg ₃ Si ₄ O ₁₂	decomp. 900	MgSiO ₃ + SiO ₂	Haraldsen (1930, p. 160).
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	820 PH ₂ O = 30,000 psi.	MgSiO ₃ + SiO ₂	Bowen and Tuttle (1949, p. 447).
Gypsum	CaSO ₄ ·2H ₂ O	dehydr. 128	CaSO ₄ ·½H ₂ O + H ₂ O	Handbook of Physics and Chemistry (1949, p. 421).
		dehydr. 163	CaSO ₄ + H ₂ O	

* All data are from Kracek (1942) unless otherwise noted.

est. For a more extensive list *see* Kracek (1942) or for more recent results, Ingerson (in press).

SOLID SOLUTIONS; EXSOLUTION TEMPERATURES

The problem of solid solutions in minerals is a complex one. A great deal remains to be done not only in determining the relation between compositions of exsolved phases but also in determining temperatures at which exsolution begins in many systems. Enough work has been done to indicate that exsolution temperatures can be very useful in geologic thermometry, especially where variation in composition of one or both phases with temperature has been determined.

Even where the exsolved phases are essentially pure compounds, or where compositions of coexisting phases have not been determined, the temperatures at which exsolution begins give minima above which the original single homogeneous phases must have formed. In Table 3 are assembled several pairs of minerals which form homogeneous solid solutions at high temperatures and unmix on cooling. The approximate temperature at which unmixing begins is indicated in each case.

Before such a temperature can have any meaning, it is necessary to establish that the observed texture was produced by exsolution. If a texture due to recrystallization or simultaneous deposition be mistaken for one due to exsolution, the interpretation will be erroneous. Schwartz (1942, p. 363-364) lists 11 criteria for the recognition of exsolution textures.

Where the composition of mix-crystals is determined by temperature an analysis of the crystals can give a much better indication of the temperature of formation. In the system FeS-ZnS, for example, the amount of FeS in sphalerite is a function of temperature of formation, if there is an excess of FeS present when the mineral is formed. Figure 1 is the equilibrium diagram of the system as determined by Kullerud (1953).

Buddington, Fahey, and Vlisidis (in press) made an analogous study of TiO₂ in magnetite associated with ilmenite. No equilibrium diagram was determined; TiO₂ was determined in magnetite from various types of igneous and metamorphic rocks

TABLE 3.—*Exsolution temperature of minerals*

Minerals	T (° C)	Reference; remarks
Digenite	78	Buerger (1941, p. 40). Either chalcocite or covellite exsolves below this temperature.
Sphalerite-chalcopyrite	350-400	Buerger (1934).
Chalcopyrite-chalcocite	480	Merwin and Lombard (1937, p. 238).
Chalcopyrite-pyrrhotite	250±	Borchert (1934, p. 150).
Bornite-chalcocite	225	Schwartz (1928, p. 397).
Ilmenite-hematite	600-700	Ramdohr (1926, p. 375).
Spinel-corundum	800±	Roy <i>et al.</i> (1953, p. 342).
Magnetite-ilmenite	600-700	Ramdohr (1926, p. 374).
Magnetite-spinel	800	Ramdohr (1925).
Magnetite-titanomagnetite (ulvö-spinel)	750	Kawai <i>et al.</i> (1954).

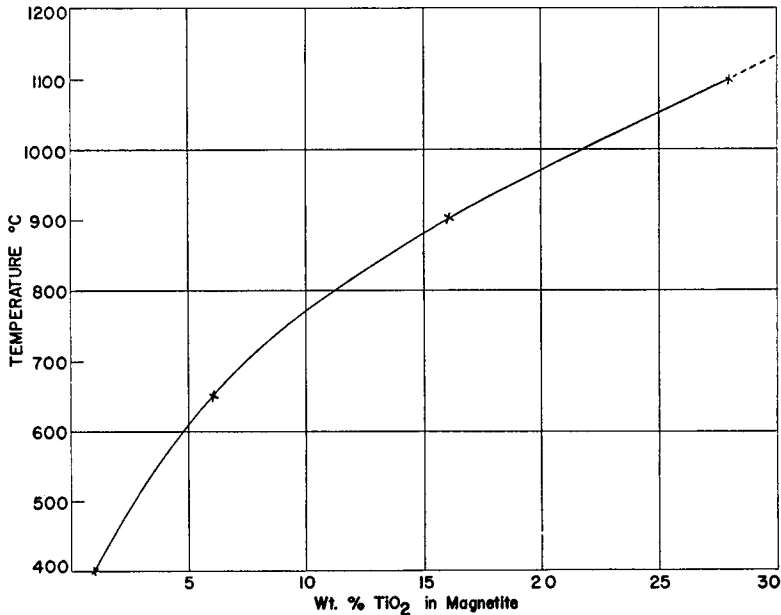


FIGURE 2.— TiO_2 in magnetite in equilibrium with ilmenite as a function of temperature

Data from a manuscript by Buddington, Fahey, and Vlisidis (in press) to be published in the American Journal of Science.

whose approximate temperatures of formation are known. The amount of TiO_2 decreases with decreasing temperature. From their summarizing table it is possible to prepare a graph which gives a rough relationship between TiO_2 content of magnetite associated with ilmenite and the temperature of formation. This graph is given here as Figure 2.

Oftedal (1943) made a study of scandium in biotite quite like that of TiO_2 in magnetite except of course that there was no Sc-rich mineral with which the biotite was in equilibrium. Oftedal found that Sc increases in biotite from low-silica through high-silica igneous rocks and pegmatites to regionally metamorphosed rocks, roughly in the order of decreasing temperature. There are no supporting experimental data, but it is possible to construct a graph similar to the TiO_2 in magnetite showing the order of magnitude of temperature of formation to be expected for biotites of various scandium contents (Fig. 3).

It is probable that the scandium content of biotite formed at a given temperature will differ from one petrographic province to another; therefore this study should be repeated for other areas.

Kuno and Nagashima (1952) determined chemical compositions of hypersthene and pigeonite which they interpreted as having formed under equilibrium conditions from a basaltic magma. From the compositions of the pyroxenes and the inversion curve determined by Bowen and Schairer (1935, Fig. 8), they estimated the temperature of crystallization (extrusion of the lava) to be $1100^\circ C$. The actual diagram used

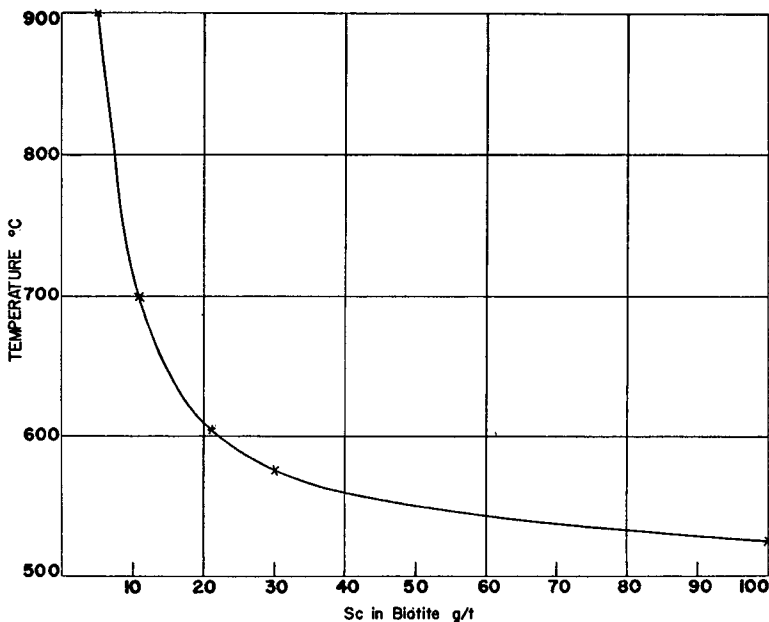


FIGURE 3.—Scandium in biotite as a function of temperature
 Drawn from data in a paper by Oftedal (1943).

(their Fig. 1, p. 1001) is a composite showing En-Fs solidus and liquidus curves as well as the inversion curve.

Feldspars.—Melting relations in the feldspars are fairly well known, the plagioclases having been studied by Bowen (1913), the alkali feldspars by Schairer (1950), and all three components by Franco and Schairer (1951). Below the liquidus, either dry or in the presence of water, the solid solution and inversion relations become so complex that they are still not thoroughly understood or agreed upon.

Barth (1951, Fig. 1, p. 147) derived a theoretical relation between temperature of crystallization and the ratio of distribution of albite between orthoclase and anorthite. Bowen and Tuttle (1950, Fig. 3, p. 497) worked out the relations experimentally. The two agree very well below about 625°C, but the maximum on Barth's curve is almost 100°C above the other and at a composition 15 atomic per cent poorer in orthoclase.

Carbonates.—Goldsmith and Graf have determined the composition of magnesian calcite in equilibrium with dolomite as a function of temperature.¹ Their experimental curve is given here as Figure 4. It is an equilibrium unmixing curve which is independent of the CO₂ pressure, except that there must be enough pressure at each temperature to prevent dissociation of dolomite.

The application in nature is to metamorphic carbonates, rather than to those of hydrothermal origin. Goldsmith and Graf have studied a variety of such carbonates and found some of them to have lamellae of magnesian calcite and dolomite, which

¹ Unpublished results; letter from Goldsmith dated Sept. 23, 1954. Details will probably appear in *Geochimica et Cosmochimica Acta* in 1955.

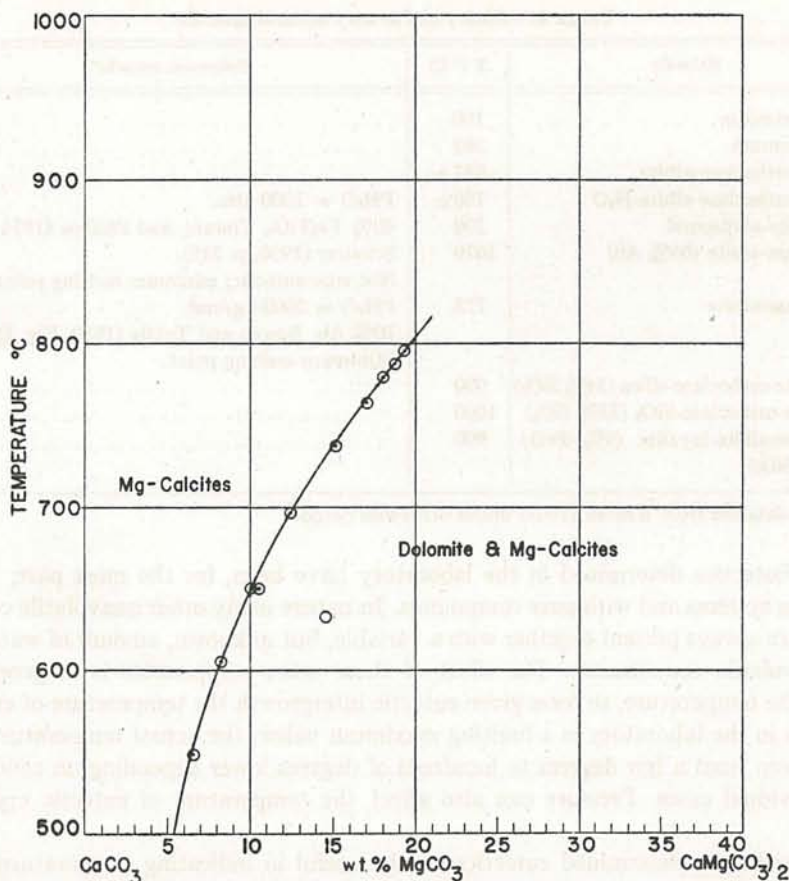


FIGURE 4.—“Unmixing curve” giving the composition of magnesian calcites in equilibrium with dolomite as a function of temperature

Unpublished data courtesy of Julian Goldsmith and Donald Graf.

they take to represent unmixing as shown by the curve of Figure 4. They suggest that such metamorphic carbonates, some of which strongly resemble perthite in appearance, are rather common but that the lamellae have been interpreted as twinning.

EUTECTICS

Eutectics could provide useful points for geologic thermometry except for two points:

(1) It is very difficult to be sure that an intergrowth of two (or more) minerals really has been produced by crystallization at a eutectic. So-called “eutectic texture” may be produced by a variety of processes, such as recrystallization, simultaneous precipitation from dilute solution, or even replacement. The first might take place at a temperature far above the eutectic; the second, much below; and the third, either above or below. Schwartz (1931, p. 762) lists five criteria that are useful in recognizing textures produced by eutectic crystallization.

TABLE 4.—Binary and ternary mineral eutectics

Minerals	T (° C)	Reference; remarks*
Sulfur-selenium	100
Silver-bismuth	262
Quartz-orthoclase-albite	937±
Quartz-orthoclase-albite-H ₂ O	750±	PH ₂ O = 1000 atm.
Magnetite-ulvöspinel	500	40% Fe ₂ TiO ₄ , Vincent and Phillips (1954, p. 8).
Orthoclase-albite (64% Ab)	1070	Schairer (1950, p. 515).
Orthoclase-albite	775	Not true eutectic; minimum melting point. PH ₂ O = 2000 kg/cm ² . 70% Ab. Bowen and Tuttle (1950, Fig. 3). Minimum melting point.
Anorthite-orthoclase-silica (54% SiO ₂)	990
Diopside-orthoclase-SiO ₂ (55% SiO ₂)	1000
Nephelite-albite-fayalite (9% FeO; 30% SiO ₂)	990

* All data are from Kracek (1942) unless otherwise noted.

(2) Eutectics determined in the laboratory have been, for the most part, in anhydrous systems and with pure compounds. In nature many other nonvolatile components are always present together with a variable, but unknown, amount of water and other volatile constituents. The effect of these other components is in general to lower the temperature, so for a given eutectic intergrowth the temperature of crystallization in the laboratory is a limiting maximum value; the actual temperature may have been from a few degrees to hundreds of degrees lower depending on conditions in individual cases. Pressure can also affect the temperature of eutectic crystallization.

Nevertheless, determined eutectics can be useful in indicating temperatures that cannot have been exceeded during final crystallization of a given mineral assemblage. In Table 4 are listed some eutectic temperatures of geologic interest, including a few determined under known pressures of a volatile constituent. Many more experimental determinations of this kind are needed, especially under different pressures of water vapor.

LIQUID IMMISCIBILITY

Liquid immiscibility probably plays little or no part in the formation of igneous rocks (Greig, 1927; 1928). Some sulfide deposits associated with igneous rocks, however, may have formed as immiscible fractions. There is some experimental evidence for such an interpretation. Olshanskii (1948), for example, found that FeS could exist as a liquid in the system FeS-FeO-SiO₂ at 800°-900°C. Presumably in a complex natural magma pyrrhotite, together with other sulfides, could remain liquid and be injected at considerably lower temperatures than those reported by Olshanskii.

A great deal of experimental work is needed on systems that approach more closely the compositions of mafic igneous rocks plus their associated sulfide ore deposits.

HYDROTHERMAL SYNTHESIS OF MINERALS

Hydrothermal syntheses can yield a great deal of information about actual temperatures of formation of many minerals in nature. The greatest experimental difficulties in hydrothermal runs are positive identification of the products and making certain that equilibrium has been attained.

The current needs in this field are: (1) a comprehensive summary of the work that has been done, and (2) phase-equilibrium work on aqueous systems both with and without other volatile components such as CO_2 , SO_2 , and halogen compounds. Several silicate and oxide systems have been studied more or less thoroughly with water, but practically nothing has been done with sulfides and other important groups of minerals.

Even in the absence of systematic data it is possible to obtain a fair idea of the temperature range over which certain minerals are stable under hydrothermal conditions.

Analcite, for example, forms readily hydrothermally at temperatures of 100° (Königsberger and Müller, 1918) to about 380°C (Ingerson, unpublished) under pressures of the order of the vapor pressures of the solutions. Under these pressure conditions *albite* forms at higher temperatures. However, this temperature boundary between analcite and albite can be raised if higher pressures of water vapor are used. For example, Yoder, (1948, p. 322-323) reports the formation of analcite at 575°C under 38,000 psi of water vapor.

Potassium feldspar ("adularia") has been formed hydrothermally at temperatures down to 245°C (Gruner, 1936).

Goldsmith and Ehlers (1952) find that *anorthite* is stable in hydrothermal solutions as low as 350°C . Below that temperature a hexagonal polymorph (unknown in nature) formed.

Folk (1947) summarized by means of diagrams the information available on laboratory alteration of feldspar. The diagram showing the effect of temperature and pH on alteration of feldspars is reproduced here as Figure 5. It gives a fairly good idea of the stability ranges of feldspar, kaolin, pyrophyllite, and muscovite (sericite) in the kinds of solutions used, and some conditions of formation of corundum and leucite are indicated.

For example, kaolin forms in acid solutions up to about 350°C if Al is high and K is low. Sericite forms from about 200° to 525°C in slightly basic to somewhat more acid solutions if Al and K are both high. Pyrophyllite forms from about 300° to 550°C if Al and K are both low.

Ewell and Insley (1935) found that coprecipitated gels of alumina and silica that formed kaolin up to 310°C gave dickite at $345\text{--}365^\circ\text{C}$ and beidellite at $360\text{--}390^\circ\text{C}$. One run at 390°C produced pyrophyllite.

Mixtures that produce kaolin in acidic or neutral solutions yield montmorillonite, over approximately the same temperature range, when the pH value is much above 7 (Noll, 1936; Eitel, 1954, p. 915). With increasing KOH, or potassium ions in the presence of other bases, potassium feldspar becomes the stable phase.

Low quartz grows readily from hydrothermal solutions rich in silica (compared to

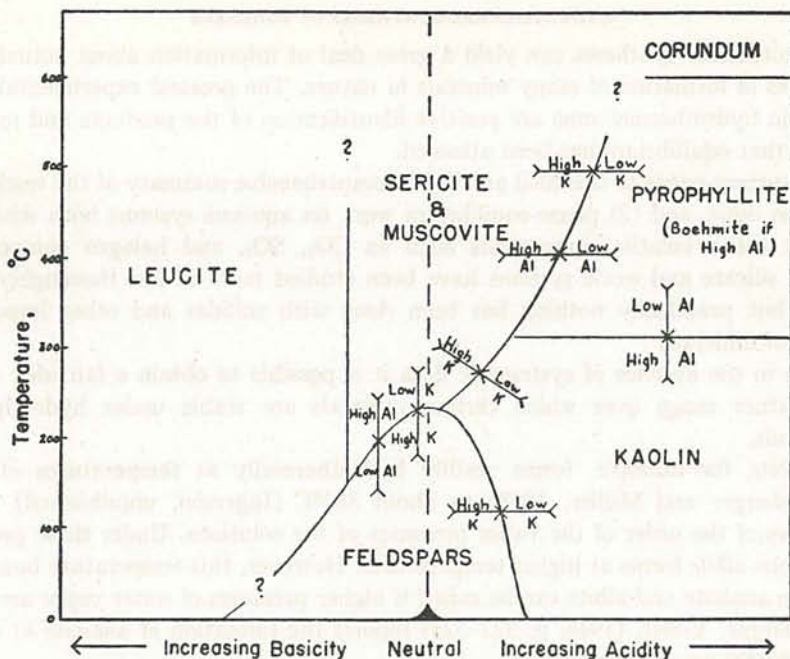


FIGURE 5.—Effect of temperature and acidity on the alteration of feldspars

After Folk (1947). Within the fields indicated for the various minerals, changes in concentration of K and Al tend to drive the boundaries in the directions shown by the arrows.

other components) from about 200°C up to its inversion temperature. Optimum conditions encountered thus far for growing large crystals are: (a) alkaline solution ($2N \pm Na_2CO_3$ solution); (b) temperature = 380°C \pm ; (c) pressure = ca. 15,000 psi (Walker, 1953).

There is no record of growth or recrystallization of quartz crystals at 100°C or lower. Silica-rich hot springs at or near 100°C deposit amorphous silica (siliceous sinter) rather than quartz. Leaching of basalt with 1 N H_2SO_4 at 50°C or less for 6 months, however, has been reported to form microcrystalline quartz from the silica remaining after the cations have been removed from the pyroxene and feldspar (Rao, 1928, p. 414).

It is probable therefore that well-formed quartz crystals even a few millimeters in size indicate temperatures of 100°C or more, and much larger crystals (some inches in diameter) are likely to have grown at 250°C or higher. Lowest temperatures found for natural quartz crystals by the liquid inclusion method are between 100° and 200°C.

Yoder and Eugster (1953) determined the stability limits of *muscovite* in terms of temperature and pressure of water vapor. Superposition of their curve on the minimum melting curve for granite of Bowen and Tuttle (1953) suggests that muscovite may form in granitic magmas above approximately 25,000 psi water vapor pressure and in the solid state below that pressure. They suggest that these relations may explain what appears to be two generations of muscovite in some granites.

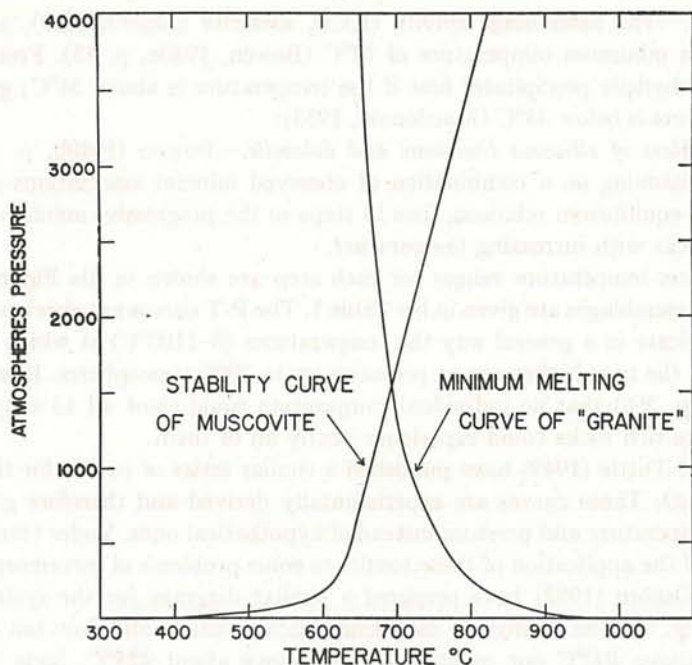


FIGURE 6.—Relation between minimum melting curve of granite (Bowen and Tuttle, 1953) and the stability curve of muscovite determined by Yoder and Eugster (1953)
Curve hitherto unpublished

The two curves are shown in Figure 6. In the experimental work sanidine, corundum, and vapor are the stable phases at temperatures above the curve. In nature sillimanite would commonly replace corundum because of the presence of free silica.

Yoder and Eugster (1954) have worked out a similar stability curve for *phlogopite* and compared it with the minimum melting curve for granite and an analogous hypothetical minimum melting curve for basalt. It appears that such a mica should be stable on the liquidus surface of the granite system at all temperatures and pressures down to about 60 atmospheres. This accords with the experience of Bowen and Tuttle (1953) who found biotite to be the primary phase in two natural granites melted under various water vapor pressures.

In rocks of the composition of basalt, on the other hand, mica would be stable only at pressures above some 40,000 psi (if the melting curve of basalt as shown is essentially correct). This also accords with experience. Yoder and Eugster (1954) cite several examples to show that biotitic mica is resorbed in low-silica igneous rocks when they come into regions of low pressure.

MINERAL ASSEMBLAGES

Mineral associations have long been used as indicators of temperatures of formation, even in the absence of experimental data. Lindgren (1936), for example, lists seven assemblages of minerals indicating in a general way temperatures of formation of hydrothermal ore deposits ranging from 600° down to about 100°C.

Evaporites.—The assemblage sylvite (KCl), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and halite (NaCl) has a minimum temperature of 72°C (Bowen, 1940a, p. 13). From natural sea water, anhydrite precipitates first if the temperature is above 34°C ; gypsum, if the temperature is below 34°C (Macdonald, 1953).

Metamorphism of siliceous limestone and dolomite.—Bowen (1940b, p. 255–257), basing his reasoning on a combination of observed mineral associations and theoretical phase-equilibrium relations, lists 13 steps in the progressive metamorphism of carbonate rocks with increasing temperature.

The pressure-temperature ranges for each step are shown in his Figure 14, and the mineral assemblages are given in his Table 1. The P-T curves are purely schematic, but they indicate in a general way the temperatures (0– 1100°C) at which each step gives way to the next higher one at pressures up to 2000 atmospheres. Bowen points out (1940b, p. 256) that no individual composition could show all 13 steps, though certain calcite-rich rocks could experience nearly all of them.

Bowen and Tuttle (1949) have published a similar series of curves for the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$. These curves are experimentally derived and therefore give actual ranges of temperature and pressure instead of hypothetical ones. Yoder (this volume) has discussed the application of these results to some problems of metamorphism.

Roy and Osborn (1952) have prepared a similar diagram for the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Fig. 7). The triangular diagrams indicate that kaolin does not appear in the system above 400°C nor montmorillonite above about 425°C , facts that were approximated above (hydrothermal synthesis) from less systematic data.

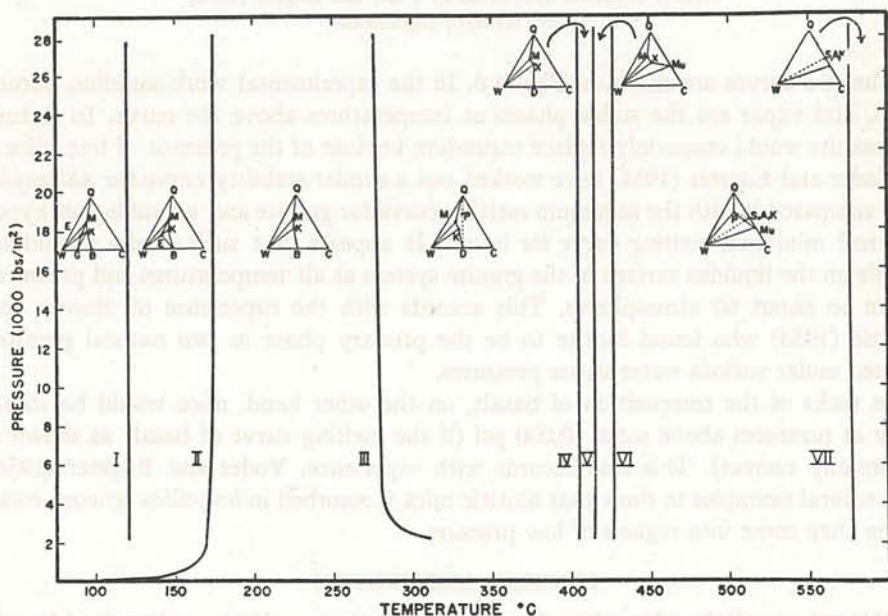


FIGURE 7.—Univariant equilibrium curves in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

After Roy and Osborn (1952). Phases: W, water; Q, quartz; C, corundum; E, endellite; K, kaolinite; X, x-phase; M, aluminian montmorillonite; P, pyrophyllite; B, boehmite; D, diaspore; Mu, mullite; SAK, sillimanite, andalusite, kyanite.

CONDUCTIVITY

Some workers have suggested that conductivity of metallic minerals varies consistently enough with temperature of formation so that this property could be used as a geologic thermometer (Smith, 1940; 1947). Other workers (*e.g.*, Hayase and Otsuka, 1952) failed to find such a relationship. The method needs more study and evaluation.

THERMOLUMINESCENCE AND DISSIPATION OF RADIATION COLORING

Many minerals and rocks that have been subjected to α -bombardment from radioactive elements in nature release the stored energy as a visible glow when heated to temperatures far below incandescence. Colors are imparted to many minerals by γ -radiation from radioactive elements. These colors are dissipated by heating, usually in the same temperature range that produces thermoluminescence.

The evidence available indicates that the activating elements are contained in the rocks (Daniels and Saunders, AT-11-1-27, chap. 12) and minerals (Holden, 1925, p. 240). Therefore, these temperatures merely mean that the minerals and rocks cannot have been heated to higher temperatures since the radiation effects were produced.

Glow curves of limestones commonly show four peaks at roughly 130°, 170°, 230°, and 300°C. Where such a limestone has been invaded by a dike, sill, or vein it may be possible, by studying glow curves in and out of the contact aureole, to determine how far the thermal effects extended and how hot the limestone was at various points.

Typical temperatures at which minerals show thermoluminescence are: fluorite, 300–400°; calcite, 60–200°; quartz, 200–300°; feldspar, 250–350°; spodumene, 225–450°C. These minerals have their radiation-induced colors dissipated in the same temperature ranges. (For details see Pringsheim, 1949; Przibram, 1953; and Headden, 1923.)

METAMICTIZATION

Minerals with relatively high contents of radioactive elements (U, Th) may have their internal structure partly or completely destroyed by continued bombardment so that they give little or no x-ray pattern. Heating recrystallizes such minerals, and the temperatures to which they must be heated indicate maxima above which they cannot have been heated since metamictization.

Most of the experimental work has been more concerned with the amount and kind of recrystallization than with determining the minimum temperature at which it will take place. Most of the recorded temperatures are above 500°C, but there is evidence that many metamict minerals would recrystallize at considerably lower temperatures if heated long enough.

EFFECTS ON INCLUSIONS AND WALL ROCKS

Temperature effects on xenoliths and wall rocks involve the same types of transformations, etc., discussed above. Larsen (1929) has cited examples, and Lovering (in press) mentions some more recent ones.

METAMORPHISM OF COAL

Where igneous bodies intrude or include coal, experimental duplication of the thermal effects on the coal allows estimates of temperature to be made. In this way

McFarlane (1929) estimated the intrusion of basalt sills at 1000°C, and Sosman (1938) of a "peridotite" (lamprophyric?) dike at 600°C.

CRYSTALLOGRAPHY

The widest use of crystallography in geologic thermometry has been in deciding whether a given mineral crystallized above or below its inversion point.

It is well known, however, that a given modification can have its crystal habit affected by temperature as well as by composition (Seifert, 1923, p. 5-7; Walcott, 1926, p. 227-239; Buckley, 1951, p. 466-467). Kalb (1923) has correlated crystal habit of several minerals with (apparent) temperatures of formation. *Calcite* is said to be tabular in high-temperature veins, steep rhombohedral or scalenohedral at low temperatures. Kalb points out that *apatite* is commonly prismatic to needlelike in igneous rocks, platy in pegmatites and veins. *Fluorite* of igneous rocks, pegmatites, and high-temperature veins, he says, is octahedral; of low-temperature veins, cubic. Dodecahedral crystals are supposed to form at intermediate temperatures.

Kalb (1924) states that crystals of potassium feldspar in porphyries (800°C±) are elongate parallel to *a*, with (001) and (010) the dominant forms; in pegmatites

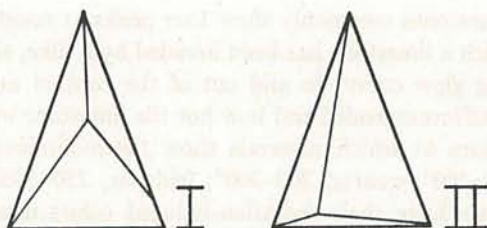


FIGURE 8.—Pattern of vicinal faces on $(10\bar{1}1)$ of right-handed low quartz

After Kalb (1933). Type I is said to occur on pegmatitic to mesohydrothermal vein quartz; Type II, on epihydrothermal quartz.

(500°C±) elongate parallel to *c*, with (010), (110), and (001) dominant; in alpine veins (350°C±), (110) more prominent and the crystals simpler; in very low-temperature veins, simple crystals with (110) and (101) only.

These generalizations appear to accord fairly well with other observations on these minerals, but Kalb's criteria (1935) for temperatures of formation of low quartz do not check with other data. The criteria are based on types of vicinal faces (Fig. 8) and presence or absence of *x*- and *s*-faces. Type Ia, usually with *x*- and *s*-faces, is supposed to indicate pegmatitic or high-temperature vein deposits; Ib, with *s*-faces, mesothermal veins; II, without *x*- or *s*-faces, epi-hydrothermal veins. Kalb, on the basis of type I vicinal faces, placed both Herkimer County and Hot Springs quartz in the relatively high temperature range (of low quartz). Both of these are generally considered to be of low-temperature origin, and liquid-inclusion measurements place the Hot Springs quartz in the 100°-200°C range.

It would appear, therefore, that this method needs (1) experimental studies of variation of crystal habit with temperature (this should be done for other minerals as well as quartz); (2) evaluation of the effect of impurities on natural and synthetic crystals.

LIQUID INCLUSIONS

In determining temperatures of mineral formation from liquid inclusions it must be assumed that:

(1) The cavities of the inclusions were filled with fluid just under the temperature and pressure prevailing during crystallization.

(2) Change of volume of the mineral itself is not significant.

(3) Changes in volume and concentration brought about by deposition of material during cooling are such as not to affect the result.

(4) Primary and secondary liquid inclusions can be distinguished under the microscope.

(5) There has been no leakage from or into the inclusions.

These assumptions appear to be justified in most cases. Exceptions must be evaluated individually.

It appears therefore that the greatest uncertainty in determining temperature of formation by observing the temperature of disappearance of the vapor phase in liquid inclusions is in estimating the pressure prevailing when the crystal was formed. This is a geologic problem whose solution can be highly accurate under favorable conditions, but little better than a guess under others.

Visual method.—In transparent minerals where inclusions can be observed in thick plates the temperature at which they become just filled with fluid can be determined visually on a heating stage or calculated from the degree of filling for inclusions of regular enough shape so that this can be determined accurately (Ingerson, 1947, p. 378).

If the pressure can be estimated a correction can be calculated from the P-V-T relations of water. The latest data are those of Kennedy (1950) whose correction curves are reproduced as Figure 9.

Decrepitation method.—For opaque minerals in which inclusions cannot be seen the decrepitation method (Scott, 1948) can be very useful, but it is subject to additional difficulties: (1) it does not distinguish between primary and secondary inclusions without independent evidence; (2) leakage during heating is not detected; (3) lag between temperature of filling of inclusions and beginning of decrepitation is highly variable from one mineral to another and cannot be evaluated directly for opaque minerals.

The liquid-inclusion method covers a temperature range where there are no fixed points of wide applicability on the geologic thermometer. It may be concluded, therefore, that in the temperature range up to about 500°C the liquid-inclusion method is at present the most widely useful one available and in general the most accurate. Isotope fractionation is more accurate, but not nearly so widely used, because of the elaborate equipment and techniques required. Moreover, it probably cannot be used at temperatures as high as 400–500°C for isotopes of most elements. Some typical results obtained from liquid inclusions are given in Table 5.

ISOTOPE RATIOS

Urey and Greiff (1935) demonstrated that it is possible to calculate the isotopic fractionation of the lighter elements that will occur at various temperatures in exchange equilibria. Epstein and others (1951) showed that actual variation of O^{16}/O^{18}

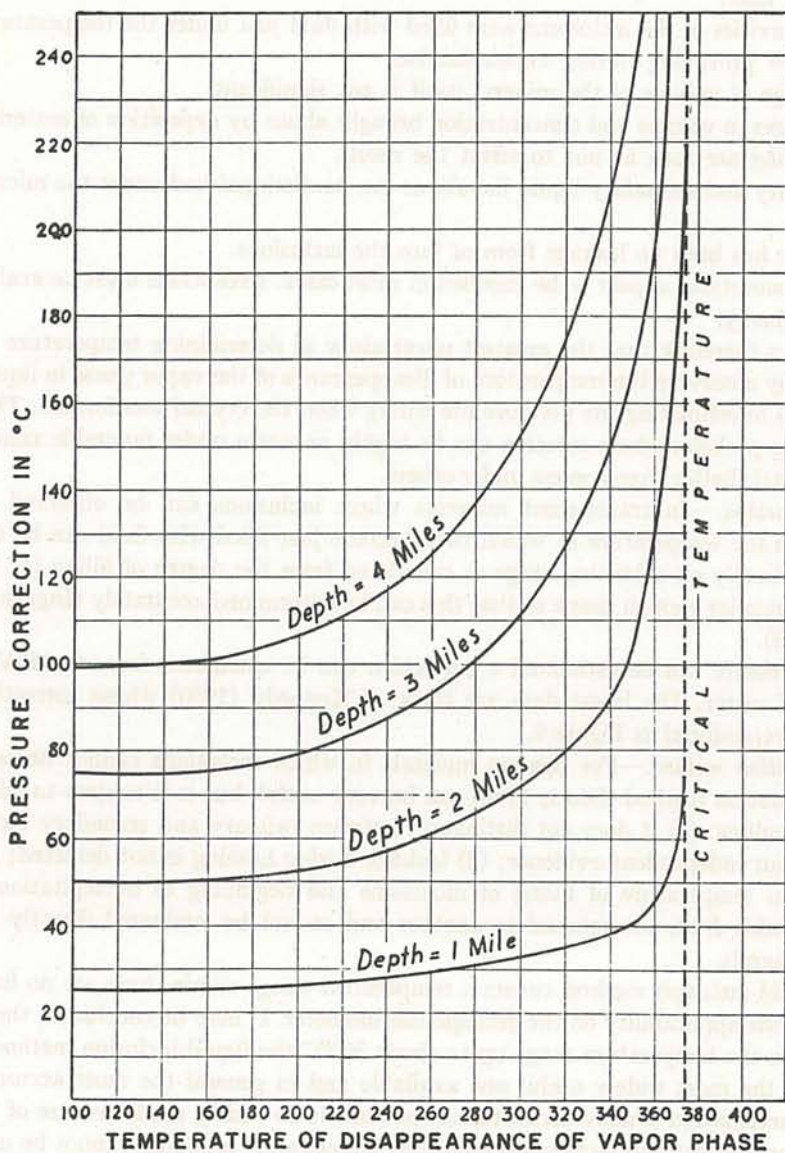


FIGURE 9.—Curves of corrections to be added to temperature of disappearance of vapor phase of liquid inclusions for various pressures at time for formation
After Kennedy (1950)

TABLE 5.—*Temperatures from liquid inclusions*

Mineral	Locality	T (° C)	Reference; remarks
Sphalerite	Upper Miss. Valley	75-121	Bailey and Cameron (1951). Pressure correction = 5-10°C.
Marcasite	Obira, Japan	279	Nishio <i>et al.</i> (1952).
Halite	Kansas	70-100	Dreyer <i>et al.</i> (1949).
Fluorite	So. Illinois	83-115	Grogan and Shrode (1952).
Fluorite	Luna Co., N. Mex.	150-202	Twenhofel (1947).
Calcite	Chihuahua, Mex.	40-50	Ingerson, unpublished results.
Calcite	Upper Miss. Valley	50-78	Bailey and Cameron (1951).
Siderite } Calcite }	Wittichen, Germany	195	Mehnert (1949). Decrepitation method. Pressure correction probably small.
Quartz	Lyangur, USSR	82-83	Ermakov (1944). No pressure correction.
Quartz	Connecticut	124-292	Cameron <i>et al.</i> (1953). Without pressure correction.
Quartz	Urals	300-420	Grushkin (1953).
Beryl	Connecticut	272-600	Cameron <i>et al.</i> (1953). Pressure correction 15,000-ft cover.
Gypsum	Ishigomari, Japan	62	Kinoshita (1924). Crystals in Tertiary volcanic tuff.
Barite	Kulikolon, USSR	119-152	Ermakov (1944). No pressure correction.

in modern shells growing at known temperatures checked closely with calculated values.

Urey and others (1951) used the empirical relation thus developed to measure growth temperatures of a series of Cretaceous belemnites from England (14°-24°C), Denmark (12°-14°C), and the southeastern U. S. (12°-18°C) from which it appears that the temperature of the Cretaceous seas was not greatly different from that of the oceans today. They also made a detailed zonal study of a large Jurassic belemnite from which it appeared that winter temperatures (15°-17°C) could be distinguished from summer ones (20°-21°C) and that the organism lived about 3 years and died in the spring.

Several different formulas have been developed; the one worked out by McCrea (1950) for the relationship between temperature and O¹⁸ content of inorganically precipitated calcium carbonate is simple and checks very well with later work on shells. It is

$$t = 18.0 - 5.44\delta$$

where t is the temperature, δ is the per mil difference between the O¹⁸ content of the unknown and of a standard gas, 18.0 is a constant characteristic of the reference gas, and 5.44 is a constant independent of the reference gas.

With marked success Emiliani (personal communication) has made a detailed study of the O¹⁶/O¹⁸ ratios in different species of *Globigerina* in deep-sea cores. Determinations on closely spaced specimens clearly reveal the post-glacial climatic maximum, minimum temperatures during glaciation, and three older glacial periods with temperature maxima and minima almost exactly the same as those of the last glaciation (Fig. 10).

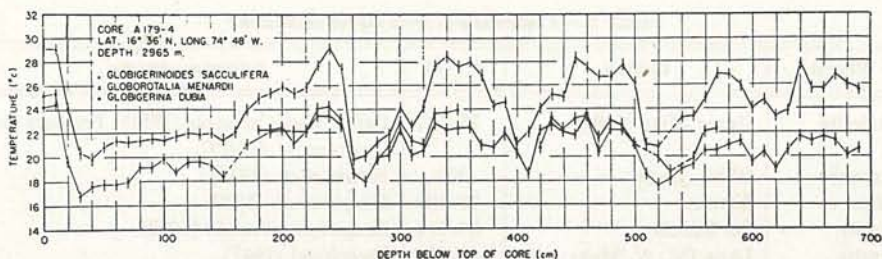


FIGURE 10.—Relation between temperature as determined by O^{16}/O^{18} ratios and depth in a deep-sea core
Hitherto unpublished data courtesy of C. Emiliani.

Study of the distribution of stable isotopes is one of the most promising methods of geologic thermometry for low to moderate temperatures. Fractionation decreases with increasing temperature and probably is nonexistent or insignificant at magmatic temperatures, but probably is significant at temperatures of epi- to meso-hydrothermal processes, at least for isotopes of the lighter elements.

SUMMARY AND CONCLUSIONS

Direct measurement of temperatures of geologic processes is the most accurate and satisfactory method but is of limited applicability.

Calculation from isotope ratios is probably the most accurate indirect method but is limited to compounds of light elements formed at low temperatures.

Liquid inclusions can give results that are accurate within a few degrees if formation pressures are accurately known, but more commonly there is an uncertainty of some tens of degrees.

Where relation between temperature and composition of exsolved phases is known, analyses of unmixed minerals can give accurate estimates of temperatures of formation. More commonly, however, exsolution phenomena merely give a minimum temperature above which an original homogeneous phase must have formed, or a range over which exsolution probably took place. Many more systems should be studied for relation between temperature and compositions of phases.

In the ideal case of a mineral assemblage formed at or very near a boundary curve it may be possible to assign a definite temperature of formation to it. In general, however, mineral assemblages indicate only ranges of temperature.

Melting points, inversions, eutectics, crystallography, and other methods mentioned commonly give only maximum, minimum, or ranges of temperature when one method is used alone, but it is frequently possible to narrow the limits considerably by using two or more methods in conjunction.

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