

Fig. 1. The present ecological zonation and relative positions of dated samples on Gaibú promontory. Heights above mean low water (datum of Brazilian Hydrographic Charts) measured with Wild level.

levels above the zone of living invertebrates. The highest and most prominent fossil zone occurs approximately 3.40 m above mean low water, 0.90 m above the highest tides, and 2.60 m above the top of the living zone. The species composition of the fossil rock is identical to that of the living zone. Weathering of the surrounding granite locally has caused limestone blocks to protrude on 2-cm high inverted conical pillars.

Other evidence of a former higher sea level is presented by an abundance of empty burrows of *Echinometra* well above its present occurrence, by fossil *Tetraclita* limestone at approximately 2.60 to 3.00 m above mean low water, and by a cemented shell beach some 2.60 m above the present beach. In protected areas, both the living zone and all the fossil zones are approximately 0.30 to 0.60 m lower than on the open promontory.

Many years ago, Branner (7) and Hartt (8) discussed evidence for a former higher position of the relative sea level along the Brazilian coast. At several of their localities, one of us (J.L.) has observed numerous empty *Echinometra* burrows and the eroded heads of the relatively deep-living corals *Montastrea cavernosa* (L.) and *Mussismilia hartti* (Verrill) well above their present locations. A dissected reef of algae and Vermetidae was observed by Ottmann (9) on the Atoll das Rocas at the 3-m sea level. Thus, the observa-

tions at Cape San Agostinho are not unique.

Radiocarbon dates obtained for four samples of limestone (10) are listed in Table 1. The samples consisted of large blocks of limestone, and great care was taken to avoid contamination. The narrow, well-defined ecological position of the living Vermetidae zone allows, by reasonable extrapolation, a definition of sea level at the time of formation with an error of no more than 0.50 m. The maximum stand observed is 2.60 m.

We conclude that in this area, one, or possibly more, oscillations of sea level have taken place in the last few thousand years. The Brazilian Shield is very stable, as are all ancient shield areas. However, the dates obtained conflict with evidence from other parts of the world, notably the Gulf Coast (11), the Netherlands (12), and Florida (13), where there is no evidence for recent sea-level stands above the present.

Recent sea-level stands higher than the stand at present have been reported by Richards and Broecker (14) for Peru and for the Caribbean coast of Colombia. In both areas, uplift appears possible. Fairbridge (2) has amassed much evidence in favor of a complexly fluctuating sea level. Two of our dates (A-17 and A-21) coincide in age with Fairbridge's Rottneest submergence and with Tavernier and Moorman's (15) Dunkirk II and III transgressions, but are a little too high. A third falls within Fairbridge's Younger Peron Terrace

(A-22). These correlations may be fortuitous and we do not wish to choose positions in the argument.

TJEERD H. VAN ANDEL  
 University of California, Scripps  
 Institution of Oceanography, La Jolla  
 JACQUES LABOREL  
 Instituto de Oceanografia,  
 Universidade do Recife,  
 Recife (Pernambuco), Brazil

#### References and Notes

1. F. P. Shepard, *Science* **143**, 574 (1964).
2. R. W. Fairbridge, *Phys. Chem. Earth* **4**, 99 (1961).
3. The samples were collected on a visit by one of us (T.v.A.) at Recife during cruise 35 of the R. V. Chain of Woods Hole Oceanographic Institution in April 1963, Contribution of Scripps Institution of Oceanography, New Series.
4. J. M. Peres and R. Molinier, Commission internationale pour l'exploration scientifique de la mer Méditerranée. Colloque tenu par le Comité du Benthos, *Rec. Trav. Stat. Marine Endoume* **13**, 22 (1957).
5. R. Molinier, *Compt. Rend.* **240**, 361 (1955).
6. Determinations by courtesy of Myra Keen, Stanford University.
7. J. C. Branner, "The Stone Reefs of Brasil; Their Geological and Geographical Relations," *Bull. Museum Comp. Zool. Harvard Coll.* **44**, Geol. Ser. 7 (1904).
8. C. F. Hartt, *Geology and Physical Geography of Brasil* (Boston, 1870).
9. F. Ottmann, personal communication.
10. The radiocarbon analyses were carried out by the Shell Development Company, Houston, Texas, through courtesy of H. A. Bernard, whose assistance is gratefully acknowledged.
11. E. McFarlan, Jr., *Bull. Geol. Soc. Am.* **72**, 129 (1961).
12. S. Jelgersma, *Holocene Sea Level Changes in the Netherlands* (van Aelst, Maastricht, 1961).
13. D. W. Scholl, *Marine Geology*, in press.
14. H. G. Richards and W. Broecker, *Science* **141**, 1044 (1963).
15. R. Tavernier and F. Moorman, *Geol. Mijnbouw* **16**, 210 (1954).

1 May 1964

#### Superconducting Metastable Compounds

Abstract. *A number of metastable phases, germanides and tellurides of gold and silver, have been prepared, analyzed by x-ray diffraction, and investigated for superconductivity. The new superconductors and their transition temperatures are AgTe<sub>3</sub> (2.6°K), Ag<sub>3</sub>Ge (0.85°K), Au<sub>3</sub>Te<sub>3</sub> (1.63°K), and Au<sub>1-x</sub>Ge<sub>x</sub> (0.99°K–1.63°K) where (0.27 ≤ x ≤ 0.60). Au-Ge compositions with other values of x do not superconduct above 0.32°K.*

The question of the universality of the superconductivity phenomenon in metals has been a matter of considerable scientific interest and controversy in recent years. The phenomenon was originally thought to be a rare and uncommon occurrence in metals, requiring just the right combination of such factors as crystal structure and

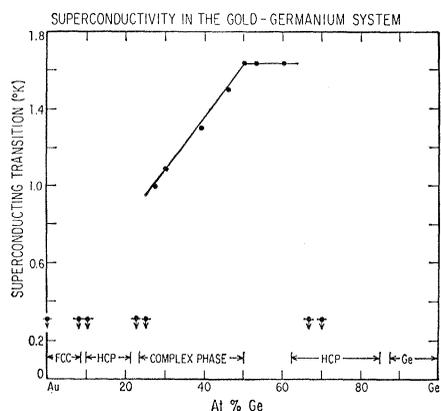


Fig. 1. Superconductivity in metastable gold-germanium compositions. The boundaries indicated for the various non-equilibrium phase fields are very approximate, and are determined from x-ray diffraction studies (10). Transition temperatures shown are upper onset temperatures. Only the complex phase is superconducting at experimentally accessible temperatures. The abbreviations are defined in the heading of Table 1.

electronic concentration, for example. As more and more superconductors have been discovered (the total number of superconducting compounds is now about 1000) (1) this view has gradually given way to the converse one, namely, that most, possibly all, metals will superconduct if the temperature is low enough (2). At present, however, this is still a matter for

speculation and study; it is by no means established that the electronic gas will condense to a superconducting state in every metal, or even in every diamagnetic metal. The problem cannot yet be discussed theoretically in a completely reliable way. Consequently, all new experimental data on previously untested compounds, particularly compounds with unusual crystal structures, atomic arrangements, or other features, are relevant.

We have prepared and examined for superconductivity a number of compounds which do not exist under conditions of thermodynamic equilibrium, but which can be prepared and retained at room temperature in a metastable state. These compounds, which have well defined crystal structures, make it possible for us to study the occurrence of superconductivity in regions of the periodic system which would not otherwise be accessible. Some of the crystal structures, moreover, are not known to occur in stable compounds.

The compounds were prepared by the rapid quenching method described by Duwez and Willens (3). This method yields a sample in the form of thin flakes of irregular geometry which are sufficiently polycrystalline to give a satisfactory Debye-Scherrer diffraction pattern. All the samples used for the measurements of super-

conductivity were x-rayed prior to the cryogenic measurements, and positive phase identification was made.

The superconducting transitions were detected by monitoring the inductance of a coil containing the sample. The frequency used was 1 kcy for some of the samples with transitions above 1.2°K, and 100 cy/sec for the others. Temperatures were measured by determining the pressure over a bath of boiling liquid helium ( $\text{He}^4$  or  $\text{He}^3$ , as appropriate) in which the samples were immersed.

The superconducting transitions of most of the compounds were quite poorly defined in temperature, which is not surprising in view of the fact that the samples were probably in a highly strained condition. The sharpest transitions had widths of 0.1 to 0.2°K; at the other extreme some samples which began to show superconductivity above 1°K (upper onset temperatures) were still not completely superconducting at 0.3°K. Table 1 shows the upper onset temperature, that is, the temperature at which superconductivity was detected. In several instances, transition temperatures were measured again after the samples had been cycled in temperatures between room temperature and 4.2°K. No changes were ever observed. None of the samples were annealed above room temperature.

In general, no great significance should be attached to the precise numerical value of the transition temperature for any particular specimen, since this is often sensitive to strain or metallurgical history (4). However, the plot of transition temperature ( $T_c$ ) versus composition for the Au-Ge compositions (Fig. 1) shows excellent internal consistency, suggesting that there are no uncontrolled metallurgical variables affecting the (upper onset) transition temperature, in this case at least.

In the Au-Ge system only the unidentified "X" phase is superconducting, at least above 0.32°K. A very small fraction of  $\text{Au}_{.90}\text{Ge}_{.10}$  and a barely detectable trace of  $\text{Au}_{.92}\text{Ge}_{.08}$  became superconducting at 0.9°K. Superconducting traces were also observed in samples with 22.5 and 25.0 atomic percent Ge, with transitions at about 0.5°K. This trace superconductivity presumably arises from small amounts of "X" phase, present in the hexagonal close packed and face centered cubic phases as a contaminant. It is interesting that  $\text{Ag}_3\text{Ge}$  superconducts (at 0.85°K) whereas the corresponding

Table 1. Superconducting transition temperatures ( $T_c$ , highest temperature of onset of superconductivity;  $T_n$ , lowest temperature at which sample is known not to be superconducting), for some metastable compounds of gold and silver. Abbreviations: HCP, hexagonal close packed; FCC, face centered cubic; "X", the crystal structure of this phase is unknown—the x-ray pattern is very complex (9); w, weak; vw, very weak; vvw, very very weak.

Sample	$T_c$ (°K)	$T_n$ (°K)	X-ray phase identification
<i>Structure defined by Luo and Klement (8)</i>			
$\text{AgTe}_3$	2.6		Primitive cubic
<i>Structure defined by Klement (9)</i>			
$\text{Ag}_3\text{Ge}$	0.85		HCP
<i>Structure defined by Lou and Klement (8)</i>			
$\text{Au}_3\text{Te}_5$	1.62		Primitive cubic
Au		0.32	FCC*
<i>Structure defined by Lou and Klement (10)</i>			
$\text{Au}_{.92}\text{Ge}_{.08}$		0.32†	FCC
$\text{Au}_{.90}\text{Ge}_{.10}$		0.32‡	FCC
$\text{Au}_{.775}\text{Ge}_{.225}$		0.32§	HCP + vw
$\text{Au}_{.75}\text{Ge}_{.25}$		0.32	"X" + vvw; FCC
$\text{Au}_{.75}\text{Ge}_{.25}$	0.99		HCP + w "X"
$\text{Au}_{.75}\text{Ge}_{.275}$			"X" + w HCP
$\text{Au}_{.70}\text{Ge}_{.30}$	1.09		"X"
$\text{Au}_{.61}\text{Ge}_{.39}$	1.31		"X"
$\text{Au}_{.54}\text{Ge}_{.46}$	1.50		"X"
$\text{Au}_{.50}\text{Ge}_{.50}$	1.63		"X" + vw Ge
$\text{Au}_{.47}\text{Ge}_{.53}$	1.63		"X" + w Ge
$\text{Au}_{.40}\text{Ge}_{.60}$	1.63		HCP + Ge + w "X"
$\text{Au}_{.38}\text{Ge}_{.62}$		0.32	vw "X" + HCP + Ge
$\text{Au}_{.30}\text{Ge}_{.70}$		0.32	HCP + Ge

\* Prepared by rapid quenching and still FCC. † Very slight trace superconducting at 0.9°K.  
 ‡ Trace superconducting at 0.9°K. § Two samples. Trace superconducting at 0.5°K in one.  
 || Trace superconducting at 0.5°K.

Au-Ge composition, crystallizing also in the hexagonal close packed structure, apparently does not, at least above 0.32°K. As shown in Table 1, AgTe<sub>3</sub> and Au<sub>3</sub>Te<sub>5</sub> were also found to be superconducting, at 2.6° and 1.6°K, respectively.

We conclude, from our results, that metastability has very little bearing on the question of whether or not a compound will become superconducting. Superconducting metastable compounds of Bi with copper (5) and various other metals (6) had been found previously by Alekseevskii and co-workers. We have found superconductivity in at least one, and probably two new crystal structures. These are the primitive (one atom per unit cell) cubic (7) structures, AgTe<sub>3</sub> and Au<sub>3</sub>Te<sub>5</sub> (the noble metal and tellurium atoms are randomly distributed over the cubic sites), and the complex undetermined phase of the Au-Ge system.

H. L. LUO

W. M. Keck Laboratory of  
Engineering Materials, California  
Institute of Technology, Pasadena

M. F. MERRIAM

D. C. HAMILTON

Department of Physics and  
Institute for the Study of Matter,  
University of California,  
San Diego, La Jolla

#### References and Notes

1. B. W. Roberts, General Electric Research Laboratory Repts. (unpublished) 63-RL-3252M (Mar. 1963); 64-RL-3540M (Jan. 1964); B. T. Matthias, T. H. Geballe, V. B. Compton, *Rev. Mod. Phys.* **35**, 1 (1963).
2. B. T. Matthias, T. H. Geballe, V. B. Compton, E. Corenzwit, G. W. Hull, Jr., *ibid.* **36**, 155 (1964).
3. P. Duwez and R. H. Willens, *Trans. AIME* **227**, 362 (1963).
4. M. F. Merriam and M. A. Jensen, *Cryogenics* **2**, 301 (1962); M. F. Merriam and M. Von Herzen, *Phys. Rev.* **131**, 637 (1963).
5. N. E. Alekseevskii, V. V. Bondar, Yu. M. Polykarov, *Soviet Phys. JETP English Trans.* **11**, 213 (1960). See also A. K. Covington, K. Groenwolt, B. W. Howlett, *J. Inst. Metals* **89**, 291 (1960).
6. N. E. Alekseevskii, N. N. Zhuravlev, I. I. Lifanov, *Zh. Eksperim. Teor. Fiz.* **27**, 125 (1954); N. E. Alekseevskii, G. S. Zhdanov, N. N. Zhuravlev, *ibid.* **28**, 237 (1955), *Soviet Phys. JETP* **1**, 99 (1955).
7. Several superconducting compounds (AuZn<sub>3</sub>, Cu<sub>18</sub>As<sub>4</sub>Sb<sub>3</sub>, LaCd<sub>13</sub>, Pd<sub>17</sub>Se<sub>15</sub>) have been indexed as primitive cubic (see 2, p. 21) but with large lattice parameters, indicating more than one atom per unit cell.
8. H. L. Luo and W. Klement, *J. Chem. Phys.* **36**, 1870 (1962).
9. W. Klement, *J. Inst. Metals* **90**, 27 (1961).
10. H. L. Luo and W. Klement, *Calif. Inst. Technol. Tech. Rept. No. 24*, AEC (Mar. 1964).
11. This work has developed from the researches of Prof. P. Duwez and B. T. Matthias, and we are indebted to them and to W. Zachariassen for advice and encouragement. We also thank A. R. Sweedler for experimental assistance. The research was supported in part by the Air Force Office of Scientific Research and the Atomic Energy Commission.

27 April 1964

7 AUGUST 1964

## Differential Estimation of Gamma-butyrolactone and Gamma-hydroxybutyric Acid in Rat Blood and Brain

**Abstract.** A sensitive and specific gas chromatographic technique for estimating concentrations of the anesthetic adjuvants,  $\gamma$ -butyrolactone and  $\gamma$ -hydroxybutyrate, in tissues has been developed. These substances do not appear to occur endogenously in either the blood or the brain of common laboratory animals. The onset and duration of anesthesia caused by the administration of either compound is correlated with the concentration of  $\gamma$ -hydroxybutyrate in the brain, rather than with that of the corresponding lactone.

Recent reports have focused attention upon the neuropharmacology and biochemistry of  $\gamma$ -butyrolactone (GBL) and the product of its hydrolytic cleavage,  $\gamma$ -hydroxybutyrate (GHB). After initial observations in this laboratory of the ability of  $\gamma$ -butyrolactone to depress the central nervous system (1) explorations of its potential use in man have been undertaken recently (2).

Fishbein and Bessman have described an isozyme of lactic dehydrogenase in mammalian brain that catalyzes the reduction of succinic semialdehyde to  $\gamma$ -hydroxybutyrate (3). Utilizing several modifications of a method that is based upon the formation of hydroxamates of esters, these investigators, contrary to the findings reported here, have claimed that both GHB and GBL are present as normal brain metabolites in a combined concentration of  $10^{-3}M$  (4). Furthermore, Bessman and Skolnik stated recently that, regardless of whether the lactone or the acid is administered to rats, the onset and duration of anesthesia are correlated with the presence of the lactone in brain and not with that of the anion (5). Our data do not support this conclusion.

A method has been developed in this laboratory for simple, rapid, direct, and specific estimation of  $\gamma$ -hydroxybutyrate and  $\gamma$ -butyrolactone in tissues, based upon the use of gas chromatography (6). By the new method one can readily detect  $10^{-6}M$  GHB or GBL in tissues. At a concentration of  $10^{-4}M$ , the recovery from blood of added GBL is 70 percent, while that from brain is 80 percent. It is clear from Fig. 1 that the retention time for GBL is comparable to that for material extracted from the brain of rats anesthetized with GBL.

In view of the report of the natural occurrence of  $\gamma$ -hydroxybutyrate and  $\gamma$ -butyrolactone in mammalian brain in a concentration of  $10^{-3}M$  (4), we have extracted and analyzed concentrates of such extracts of rat brain and blood, rabbit brain, cat brain, and dog

blood for total GBL and GHB contents. None of the tissues was found to contain these substances. While it is conceded that the lactate dehydrogenase of brain can reduce succinic semialdehyde to GHB, our results suggest

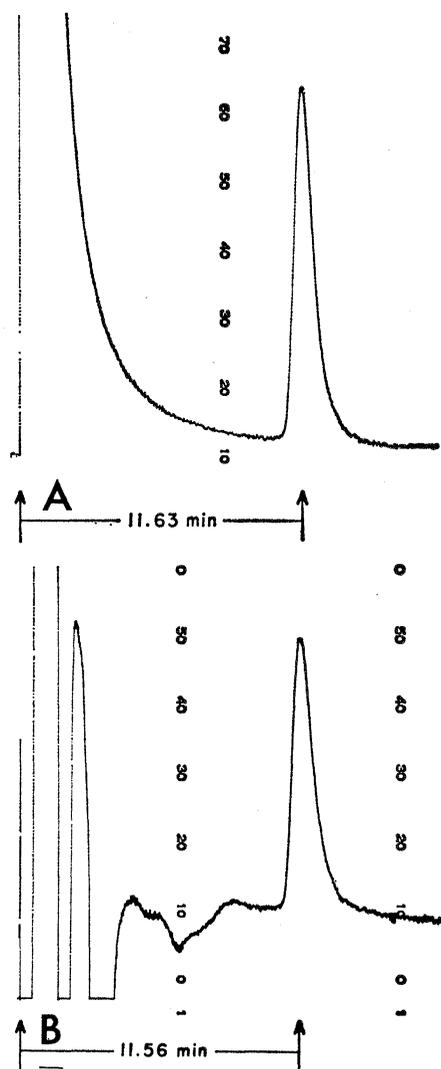


Fig. 1. Gas chromatograms of (A) authentic GBL and (B) of an extract of brain of an animal anesthetized with GBL prepared as described (6). The irregularity at the beginning of record B is caused mainly by the trichloroacetic acid in the extract. This can be removed by adsorption with Dowex-2 chloride; it has been found, however, that the presence of trichloroacetic acid does not alter the retention-time of GBL on the column.