needs. The Navy program requires a substantial course in physics; the Army program is such as to increase above normal the number of students electing physics. On the basis of joint announcements of the services and conferences with their representatives, the committee has estimated that the teaching load in college grade physics will in 1942–43 be from two to three times the highest ever before sustained. This teaching load will fall on faculties necessarily depleted for war research and, in some instances, wastefully dissipated through the direct action or indirect influence of the Selective Service Act and the lack of knowledge in some local boards as to the importance of physics and its wartime role.

The committee welcomes the very specific directives which have been issued by Selective Service Headquarters, but urges that high officials of the Army and Navy issue statements emphasizing the necessity for students and teachers to continue their present work and affirm that in so doing the individuals concerned are performing the highest and most patriotic duty open to them. Such public statements, as well as occupational deferment policies, should particularly include graduate students, since these students are already contributing heavily to the teaching of physics and are being drawn more and more into war research.

Whatever actions may be taken by federal authorities (and some are known to be in preparation) designed to lessen the prospective shortage of teachers, the committee is convinced that they can not be wholly adequate. The committee, therefore, urges college and university administrations and faculties to use every expedient they can devise to prepare for the coming flood of enrolments in physics courses. This advice is all the more urgent in view of the fact that the war research programs must continue to expand and that additional faculty members will have to be called away from their teaching duties.

# SPECIAL ARTICLES

## RELATIONSHIPS OF THE HIGHER ARSENIDES OF COBALT, NICKEL AND IRON OCCURRING IN NATURE

THE interrelations of the higher arsenides of cobalt, nickel and iron has long constituted a mineralogical problem. An extended series of studies has been conducted in an attempt to arrive at a better understanding of this group. In this investigation minerals from numerous localities have been examined microscopically and by means of x-rays, and as many as possible of the compounds have been produced synthetically. Some time will necessarily elapse before a complete report is published. In the meantime, it is hoped that this brief account may provide a useful outline.

Previous attempts at synthesis reveal few claims to the production of the higher arsenides of these metals. Many of the conclusions reached are also in doubt, since the experiments were carried on more than a quarter century ago, and the materials produced were identified without the aid of either the reflecting microscope or x-ray diffraction. In the absence of such methods it was neither possible to establish the homogeneity of the product nor to identify the phases obtained.

The present investigation has been carried on in the mineralogical and x-ray diffraction laboratories of the Department of Geology at Columbia University. The author takes pleasure in expressing his sincere appreciation for the unfailing encouragement, advice and helpful criticism of Professor Paul F. Kerr, of this institution, at whose suggestion the investigation was undertaken. The method of synthesis employed throughout has been that of dry fusion. X-ray powder diffraction methods utilizing both Debye and Bohlin-Phragmen cameras with iron radiation have been employed in the determination of the homogeneity of the product, in the identification of the phases present and in the correlation of the synthetic and natural material. The x-ray data have been confirmed in many cases by the use of the reflecting microscope.

*Orthorhombic Arsenides* $RAs_2$

Safflorite
Löllingite
Rammelsbergite
Pararammelsbergite

Synthetic equivalents of rammelsbergite, pararammelsbergite and löllingite have been for the first time identified with the natural minerals by means of x-ray diffraction. The synthesis of "safflorite" was unsuccessful except when iron was employed in addition to cobalt, this cobalt-iron material giving a diffraction pattern of the safflorite type. Patterns of natural safflorite and the synthetic cobalt-iron compound are similar to those of löllingite. Furthermore, no orthorhombic diarsenide of pure cobalt has been reported in nature nor has it at any time been prepared synthetically. All analyses of the mineral safflorite are high in iron. Safflorite should be redefined as a cobaltiferous löllingite and has doubtful merit as an independent species.

*Isometric Arsenides*

| $RAs_2$ | $RAs_3$ |
|---|---|
| (*Smaltite) | Skutterudite |
| (*Chloanthite) | Nickel Skutterudite |
| (*Arsenoferrite) | Iron Skutterudite |

* (Discredited)

Although many published analyses of these minerals roughly approximate the composition $R:As_2$ others vary widely in arsenic content, indicating a range from approximately $R:As$ to $R:As_3$. The assumption of the existence of two distinct series, one of diarsenides of cobalt, nickel and iron, respectively (smaltite-chloanthite-arsenoferrite), the other of triarsenides (skutterudite-nickel skutterudite-iron skutterudite) is a consequence of this variability in metal-arsenic ratio. Since few specimens have approached the $R:As_3$ ratio, some mineralogists have considered the diarsenides to constitute the only valid group and have looked upon the skutterudites as arsenic rich varieties of the diarsenides. Another feature which must be considered in any discussion of the interrelations of these minerals is the extensive isomorphous substitution among the three metallic elements, a phenomenon that has long been recognized.

Oftedahl established the crystal structure of skutterudite employing the assumption that the formula was $R:As_3$ and demonstrated that the x-ray data could be reconciled with this composition, but was in no way compatible with a composition $R:As_2$. However, he left unanswered the explanation of the anomalous situation in which it appears that diarsenides and triarsenides of the same metals possess identical crystal structures. He also offered no satisfactory evidence to explain the variation in lattice constants shown by the natural isometric arsenides or the variable arsenic content indicated by the published analyses. The present investigation has had as one of its primary purposes the clarification of this situation.

Study of the naturally occurring isometric arsenides coupled with experiments in synthesis suggests that the so-called isometric diarsenides smaltite-chloanthite-arsenoferrite should be discredited as valid mineral species and the name skutterudite should be substituted for the entire group of isometric arsenides of cobalt, nickel and iron. This appears to be the only satisfactory solution of the apparently anomalous situation in which diarsenides and triarsenides of the same metals possess the same crystal structure. The variations in lattice constants and arsenic content shown by the natural arsenides may be satisfactorily accounted for under this revised view of the relationships of these minerals. The reasons for the above conclusions may be enumerated as follows:

(1) Published analyses of these minerals only approximate the theoretical metal-arsenic ratio $R:As_2$ and exhibit wide divergence in both directions approaching $R:As$ and $R:As_3$.

(2) The majority of published analyses were made many years ago and are of questionable reliability, since neither microscopic nor x-ray methods were employed in establishing the homogeneity of the analyzed material.

(3) Oftedahl, using only one specimen each of smaltite and chloanthite, established the essential identity of structure of these minerals with that of the triarsenide skutterudite. This has been amply confirmed in the present investigation employing many specimens of so-called diarsenides from a large number of localities.

(4) Furthermore, it was established by Oftedahl that the x-ray diffraction data provided by the natural arsenides of these metals is only compatible with the composition $R:As_3$ and can not be reconciled with a composition $R:As_2$.

(5) Cobalt triarsenide and a series of triarsenides isomorphous with it containing varying amounts of the metals cobalt, nickel and iron have been successfully synthesized in the course of the present investigation, whereas attempts to synthesize isometric diarsenides of these metals have been unsuccessful.

(6) The natural isometric arsenides exhibit a variation in lattice constants which is of approximately the same range as that shown by the synthetic isometric arsenides. Since the variation in lattice constants of these synthetic compounds is dependent on mutual substitution among the three metallic elements cobalt, nickel and iron, it seems likely that the same may be true in the case of the natural minerals. Previous suggestions of others that the substitution of metal for arsenic may account for this phenomenon are not supported by the present investigation.

(7) Microscopic examination of many specimens of smaltite and chloanthite demonstrates that the low and variable arsenic content of the so-called diarsenides can be accounted for, in many cases at least, on the basis of mechanically admixed lower arsenides. Wide-spread lack of homogeneity is evident. Niccolite, rammelsbergite and other lower arsenides frequently appear within apparently homogeneous crystals of the isometric arsenides. No evidence of metal for arsenic substitution was observed among the synthetics although the subject has not been exhaustively investigated. Even should it be established that metal for arsenic substitution exists in certain cases, the fundamental basis for the recognition of the so-called diarsenides as valid species is not strengthened, since they possess a crystal structure shown by Oftedahl to be compatible only with the composition $R:As_3$. In the former case they would be impure skutterudites, in the latter arsenic poor skutterudites but skutterudites they remain.

The present classification, theoretical compositions and crystal systems of the principal naturally occurring higher arsenides of these metals and a revised classification based in part on the results of these experiments in synthesis are shown below.

| *Previous Classification* | *Composition* |
|---|---|
| Orthorhombic Arsenides | |
| Safflorite | $CoAs_2$ |
| Rammelsbergite | $NiAs_2$ |
| Pararammelsbergite | $NiAs_2$ |
| Löllingite | $FeAs_2$ |
| Isometric Arsenides | |
| Diarsenides | |
| Smaltite | $CoAs_2$ |
| Chloanthite | $NiAs_2$ |
| Arsenoferrite | $FeAs_2$ |
| Triarsenides | |
| Skutterudite | $CoAs_3$ |
| Nickel-skutterudite | $NiAs_3$ |
| Iron-skutterudite | $FeAs_3$ |

| *Revised Classification* | *Composition* |
|---|---|
| Orthorhombic Arsenides | |
| *Cobalt-löllingite (Safflorite) | $(CoFe)As_2$ |
| Rammelsbergite | $NiAs_2$ |
| Pararammelsbergite | $NiAs_2$ |
| Löllingite | $FeAs_2$ |
| Isometric Arsenides | |
| Diarsenides (Discredited) | |
| Smaltite (Identical with skutterudite) | |
| Chloanthite (Identical with nickel-skutterudite) | |
| Arsenoferrite (Identical with iron-skutterudite) | |
| Triarsenides | |
| Skutterudite | $CoAs_3$ |
| *Nickel-skutterudite | $(CoNi)As_3$ |
| *Iron-skutterudite | $(CoFe)As_3$ |

* Indicates pure mono-metallic end member neither satisfactorily established as occurring in nature nor produced synthetically.

For the first time the existence of the orthorhombic minerals rammelsbergite, pararammelsbergite and löllingite as arsenides of the pure metals has been confirmed by the results of synthesis and x-ray studies. Consideration of the data for both natural and synthetic "safflorite" provides no evidence of the existence of a pure orthorhombic cobalt diarsenide and suggests that this mineral might be considered a cobaltiferous löllingite rather than an independent species.

In view of the previous discussion it would seem that the names smaltite, chloanthite and arsenoferrite, which have long been applied to minerals accepted as isometric diarsenides of the elements cobalt, nickel and iron, respectively, no longer serve any useful purpose. In fact, their retention in the literature tends to confuse our view of the relationships of the isometric arsenides of these metals, all of which are apparently structurally triarsenides whether or not they can be shown to possess the exact chemical composition demanded by the $R:As_3$ ratio.

Furthermore, it would seem that the name skutterudite should be applied to the entire group of isometric arsenides of cobalt, nickel and iron, since the cobalt triarsenide is the most firmly established of all the isometric arsenides of these metals. In the course of the present investigation it has been synthesized and the identity of the synthetic product and the natural mineral skutterudite established for the first time. The same investigation has established the existence of a three-fold isomorphous series of isometric triarsenides ($CoAs_3$-$NiAs_3$-$FeAs_3$) in which the elements cobalt, nickel and iron substitute for each other in various proportions. The nickel and iron end members of this series have not been synthesized; neither has their existence in nature been satisfactorily established. The precise limits of substitution of the three metals in the series are yet to be determined. Inasmuch as pure nickel and pure iron end members are missing there is little justification for assigning them special names. It would seem preferable to apply the appropriate prefix, as has already long been done in the case of nickel skutterudite for the high nickel, high iron or high nickel and iron varieties.

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## EFFECT OF MUCIN ON INFLUENZA VIRUS INFECTION IN HAMSTERS[1]

In a study of factors which decrease the resistance of experimental animals to virus respiratory infections, the effect of the intratracheal inoculation of hamsters (*Cricetus auratus*) with influenza A virus in mucin has been determined.

The hamster was selected as the test animal because it appeared, from Taylor's work,[2] to have a limited susceptibility to this virus, as evidenced by failure to develop gross lesions. Mucin was used, since it has been shown to lower resistance to bacterial infections;[3] further, the possible role of mucous secretions in decreasing resistance to infections of the respiratory tract in general has been the subject of several papers by our group.[4,5,6]

### Method

The PR-8 strain of influenza A virus[7] was main-

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[1] This work was aided by a grant from The Kresge Foundation.

[2] R. M. Taylor, *Proc. Soc. Exp. Biol. and Med.*, 43: 541, 1940.

[3] W. J. Nungester, A. A. Wolf and L. F. Jourdonais, *Proc. Soc. Exp. Biol. and Med.*, 30: 120, 1932.

[4] W. J. Nungester and L. F. Jourdonais, *Jour. Infect. Dis.*, 59: 258, 1936.

[5] W. J. Nungester and R. G. Klepser, *Jour. Infect. Dis.*, 63: 94, 1938.

[6] W. J. Nungester, R. G. Klepser and A. H. Kempf, *Jour. Infect. Dis.*, in press.

[7] Obtained through the courtesy of Dr. Thomas Francis, Jr.