Mineralogical Magazine, October 2001, Vol. 65(5), pp. 685–687

Dienerite – a mystification

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ABSTRACT

The mineral name dienerite should be allowed to slip into obsolescence. Dienerite $AsNi_{3-x}$ is probably nickelskutterudite $As_{3-x}Ni$ caused by a typographical error in the chemical analysis.

KEYWORDS: dienerite, obsolete mineral name, nickelskutterudite.

Introduction

AFTER the publication of the last edition of the Mineral Powder Diffraction File by Bayliss *et al*. (1992), a continuing effort has been made to find or collect X-ray powder diffraction data of all valid mineral species for the next edition, Bayliss *et al*. (2001).

An unnamed mineral was found by Austrian palaeontologist Professor Carl Diener (1862–1928) in a now abandoned mine, Radstadt, Salzburg, Austria. Hackl (1921) described this unnamed mineral as fine, ½ cm cubes with greyish-white colour and metallic lustre similar to chloanthite (now called nickelskutterudite). The chemical analysis is given as As 30.64, Fe 0.61, Co 1.29, Ni 67.11, Cu 0.99, Ag 0.01655, and trace S, which totals 100.66. From the As:Ni = 2.80, the formula was deduced as $AsNi_3$, which has As 29.87 and Ni 70.13. This mineral, if homogeneous, was named as dienerite, after the original discoverer, by Doelter (1926).

The mineral data compilations in the last decade are the Mineralogy database (*http://www.webmineral.com*), *Glossary* (Mandarino, 1999), *Lapis Mineralienverzeichnis* (Weiß, 1998), *Dana* (Gaines *et al*., 1997), *Hey's Index* (Clark, 1993), *Manual* (Nickel and Nichols, 1991), *Encyclopedia* (Roberts *et al*., 1990) and *Handbook* (Anthony *et al*., 1990). All compilations list dienerite in bold face (species status) with only the *Manual* adding a "Q" for questionable. Although dienerite was missing from the *Encyclopedia* (Blackburn and Dennen, 1977) it was added as a correction in the update by Martin and Blackburn (1999). At this point, the project looked very simple. Even very poorly crystalline cubic minerals yield star quality X-ray powder diffraction data, because the space-group aspect is easily obtainable.

Occurrence

Ramdohr (1969) states that the only reported specimen is lost. The catalogues of many museums were checked, and many letters to museum curators were written without success. All replies were negative, including that from Dr. G. Niedermayr, Naturhistorisches Museum Wien, Austria (pers. comm., 1986). He states "... I am sure that there is no specimen of dienerite in existence from the locality where it had been found for the first time – maybe it's a mystification, ...".

It appears that Prof. Carl Diener sent the whole specimen to the chemical laboratory of the State Geological Survey. The specimen (>20 g) was used completely in the very accurate determination of Ag.

The mineral was described in 1921, which means that there have been 80 years to find a second specimen. The simple and common chemistry of Ni-As (hundreds of Ni-As deposits) and the relatively large size of the specimen described suggest that a second specimen or a second occurrence should have been found in this 80 year time interval.

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Chemistry

Descamps (1878) gave an early report of synthetic $AsNi_3$; however, Hansen and Anderko (1958) state "Ni_3As and Ni_2As have been proved nonexistent." The $AsNi_3$ compound does not appear in the synthetic phase diagram. Gervilla *et al*. (1994), who investigated the system Pd-Ni-As at 790 and 450°C, state "our data confirm the currently accepted picture of the Ni-As system (Yund, 1961, 1962)...".

The closest structural analogues would be $AsCo_3$ and $AsFe_3$; however, neither Villars and Calvert (1991) nor a literature search of the Powder Diffraction File (2000) produced a cubic analogue.

Crystal structure

Since the crystal system is cubic and the atoms would be almost neutral, the expected crystal structure should be cubic close packed. Such a crystal structure, which involves a mix of three small atoms (Ni) with one large atom (As), is unlikely

Domeykite, $AsCu_3$, is cubic $I\bar{4}3d$ with a = 9.619 Å (Iglesias and Nowacki, 1976). The metal elements are Fe 0.61%, Ni 67.11%, Co 1.29%, Cu 0.99% and Ag 0.01655%. Elements such as Cu and Ag would stabilize a crystal structure with 4-2 coordination. The ratio of Fe+Ni+Co:Cu+Ag is 68. Such a number of 4-2 coordination atoms (Cu+Ag) is insufficient to stabilize a crystal structure.

Discussion

The policy of the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association is to formally discredit a mineral if a type or cotype specimen is examined (Dunn, 1990). The reason for this sensible policy is that CNMMN could receive a veritable flood of such proposals without any scientific work being done, because there are tens of thousands of obsolete names in the literature (Bayliss, 2000). Since neither a type or cotype exist, the mineral cannot be formally discredited.

What potential old mineral species are missing from the Mineral Powder Diffraction File? There are a number of amphibole minerals, because the mineral nomenclature keeps changing and some of the CNMMN-approved mineral names are probably chemical varieties. There are a number of amorphous minerals, because they are not adequately described like opal and evansite. Of the dozen potential mineral species remaining, dienerite is unique in that its existence is questionable.

From the synthetic phase diagram, this chemical analysis represents about a 1:1 mixture of nickel:orcélite (As_2Ni_{5-x}). This is unlikely, because fine, ½ cm cubes would not contain equal portions of two minerals with different crystal systems, if heterogeneous.

Could the mineral be difficult to prepare in the laboratory? Usually such minerals involve slow order-disorder transformations like gersdorffite, AsNiS. Dienerite does not fall in this category. The simplicity of the quoted chemical formula and cubic symmetry indicates that dienerite does not form, because there are no probable crystal-structure models.

There are five recently discredited minerals (Peacor *et al*. 1982). 'Texasite' and 'albrittonite' exist only as synthetic phases. 'Cuproartinite' and 'cuprohydromagnesite' are not known to exist in any form. 'Yttromicrolite' is a heterogeneous mixture. Is dienerite a description by a *bona fide* scientist? The mineral find by one person; the mineral description by a second person; and the mineral name by a third person five years later strongly suggest scientific integrity.

If the percentage of As and Ni were accidentally interchanged, then the composition, $As_{3-x}Ni$, represents nickelskutterudite. The physical description of greyish-white colour with metallic lustre and an occurrence of fine ½ cm cubes is quite realistic for nickelskutterudite.

The mystery of dienerite must remain unsolved, but the name should be allowed to slip into obscurity..... unless, of course, someone is able to come up with convincing evidence to the contrary.

Acknowledgements

N. Cook, R.F. Martin, E. Nickel and H. Strunz are thanked for helpful comments.

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[*Manuscript received 9 December 1999: revised 27 August 2001*]