TRIGONAL AND CUBIC FE2SI POLYMORPHS (HAPKEITE) IN THE EIGHT KILOGRAMS FIND OF NATURAL IRON SILICIDE FROM GRABENSTÄTT (CHIEMGAU, SOUTHEAST GERMANY): F. Bauer¹, M. Hiltl², M. A. Rappenglück³, K. Ernstson⁴. ¹Oxford Instruments GmbH NanoScience, Wiesbaden, Germany (frank.bauer @oxinst.com), ²Carl Zeiss Microscopy GmbH, D-73447 Oberkochen, Germany (mhiltl@online.de), ³Institute for Interdisciplinary Studies, D-82205 Gilching, Germany (mr@infis.org), ⁴Faculty of Philosophy I, University of Würzburg, D-97074 Würzburg, Germany (kernstson@ernstson.de).

Introduction: Some 30 years ago a metallic, silvery gleaming boulder weighting 8 kg (Fig. 1) was excavated near the town of Grabenstätt on Lake Chiemsee in Bavaria. As an enigmatic object of completely unknown origin the private finder bequeathed it to the family where it fell into oblivion.



Fig. 1. The eight kilograms iron silicide boulder from Grabenstätt. Centimeter scale. Fig.2. Location map for the Chiemgau impact crater strewn field and iron silicide occurrences.

The find was brought to mind again when similarly looking metallic matter became common currency in the Chiemgau district as basically important for the meanwhile established Chiemgau meteorite impact event. Here we report on detailed analyses of the boulder that rapidly proved to be iron silicide matter thus remarkably adding to the iron silicides family from the Chiemgau crater strewn field so far established and published [1-5].

Iron silicides and the Chiemgau meteorite impact event: The discovery of the Chiemgau meteorite crater strewn field was directly paralleled by the abundant finds of iron silicides comprising gupeiite, xifengite, hapkeite, naquite and linzhite, and containing various carbides like, e.g., moissanite SiC, titanium carbide TiC and khamrabaevite (Ti,V,Fe)C, and calcium-aluminum-rich inclusions (CAI), minerals krotite and dicalcium dialuminate (Fig. 3). With regard to this exotic mineral assemblage and the extreme purity of the carbide crystals that obviously was not achieved under terrestrial conditions, an industrial or a geogenic origin was discarded, in particular with regard to the very specific sampling situations. Hence a cosmic origin got increasing evidence. So far the total mass of the iron silicides has amounted to about two kilograms sampled from the whole strewn field with metal detectors, and the largest specimen was a few centimeters tall and weighed 160 g. Against this background the recovery of an iron silicide "monster" from the crater

strewn field weighting eight kilograms proved to become a scientific stroke of luck.

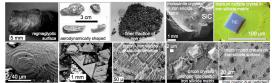


Fig. 3. Various aspects of iron silicides from the Chiemgau meteorite impact crater strewn field.

Methods: From the strongly magnetic boulder splinters of thumbnail size were removed and provided with mirror polish for SEM-EDX and EBSD analyses, and Raman spectroscopy.

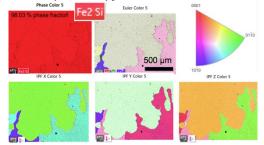


Fig. 4. EBSD reveals nearly 100 % Fe_2Si with conspicuous grain boundaries (see text).

Results: From the EBSD analyses of one boulder splinter (Fig. 4) the general texture proved to be Fe₂Si making the main mass (98,3 % phase fraction). The phase description for the Fe₂Si is the trigonal crystal system [7, 8]. The reniform contact of the four differently oriented grains far from any crystallographic direction is enigmatic, because they are not growth-related and not related to recrystallization either. They rather point to interpenetration from a rapidly quenched formation or to a similar process of metasomatic overprint.

Within the Fe₂Si matrix tiny inclusions with sizes between a few micrometers and about 1 mm are scattered forming two different clusters as seen in the EDS Layered Image (Fig. 5). It established one cluster to be formed of pure carbon particles, and Raman spectroscopy identified graphite (Fig. 6 A, 7) with typical D, D' bands of disordered graphene. The second cluster revealed a larger variability, and EBSD suggest gupeiite, khamrabaevite and possibly zirconium carbide contributing to the inclusions (Fig. 4, Fig. 6 B). A certain amount of uranium could not be ascribed to a reasonable compound. At a second position of the 8 kg block, titanium carbide/khamrabaevite and carbon inclusions were established in a matrix of cubic hapkeite and cubic gupeiite.

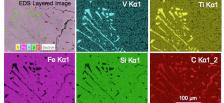


Fig. 5. EDS reveals two clusters of inclusions within the iron silicide matrix: irregular orientation of carbon particles and aligned particles near to khamrabaevite, (Ti,V,Fe)C.

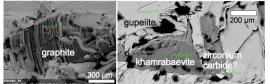


Fig. 6. Inclusions within the iron silicide matrix. Graphite has been established by Raman spectroscopy (Fig. 7). EDS data suggest gupeiite, khamrabaevite and possibly zirconium carbide.

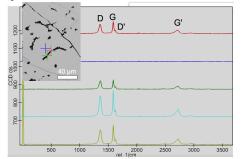


Fig. 7. Raman spectra taken at the cross positions: typical graphite spectrum with D, D' bands of disordered graphene.

Discussion: In the literature a trigonal (P3-m1), and a tetragonal (Pm3-m) Fe₂Si polymorph are described [9-12] after a first artificial preparation of Fe₂Si (unclear polymorph) in 1939 [13]. A cubic polymorph, especially named hapkeite-1C for its first detection in the lunar Dhofar 280 meteorite [14, 15], was later also discovered in a sample from the Luna 24 Mare Crisium landing site [16] and in an Apollo 16 regolith sample [17]. Recently hapkeite $(1-2 \mu m)$ was found in a meteorite from Koshava, Bulgaria, [18] and also discovered in the meteorite DAG 1066 [19] and occurs in a grain from the FRO 90228 ureilite [20]. Fe₂Si reported for magnetic spherules in Hungary could be related to cosmic dust or a meteorite impact [21]. Hapkeite was found also in a 7µm Supernova graphite (OR1d3m-18) from the Orgueil meteorite

[22]. The trigonal polymorph – the most stable among the silicides (up to 255 GPa) – in conjunction with xifengite (Fe₅Si₃), gupeiite (Fe₃Si), and inclusions of cubic SiC (moissanite) and (Ti,V,Fe)C (khambraevite), was discovered in a sample coming from the Chiemgau Impact area [3]. These findings show that Fe₂Si is produced by (1) extreme reduction and shock heating in an impact melt, (2) condensation of a silicate vapor caused by a massive impact event, and (3) space weathering. The reported Fe₂Si in a fulgurite [23] is mentioned for reasons of completeness._Only now Fe₂Si (all polymorphs) come into focus for industrial application.

Conclusions: From these analyses and within the specific context – an 8 kg chunk of massive iron silicide containing Fe₂Si in close proximity to the Lake Tüttensee meteorite crater in the Chiemgau impact strewn field, no artificial production and no fulgurite – it is very probable that the boulder is of extraterrestrial origin. Hitherto it is the biggest sample known to contain natural Fe₂Si in its cubic phase (hapkeite-1C), and together with the earlier reported polymorph [3] the first natural occurrence of trigonal Fe₂Si. For reasons of definiteness we suggest to name the trigonal Fe₂Si polymorph hapkeite - 2T possibly rating a new mineral name.

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