Trigonal and cubic Fe_2Si polymorphs (hapkeite) in the eight kilograms find of natural iron silicide from Grabenstätt (Chiemgau, Southeast Germany)

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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.

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].

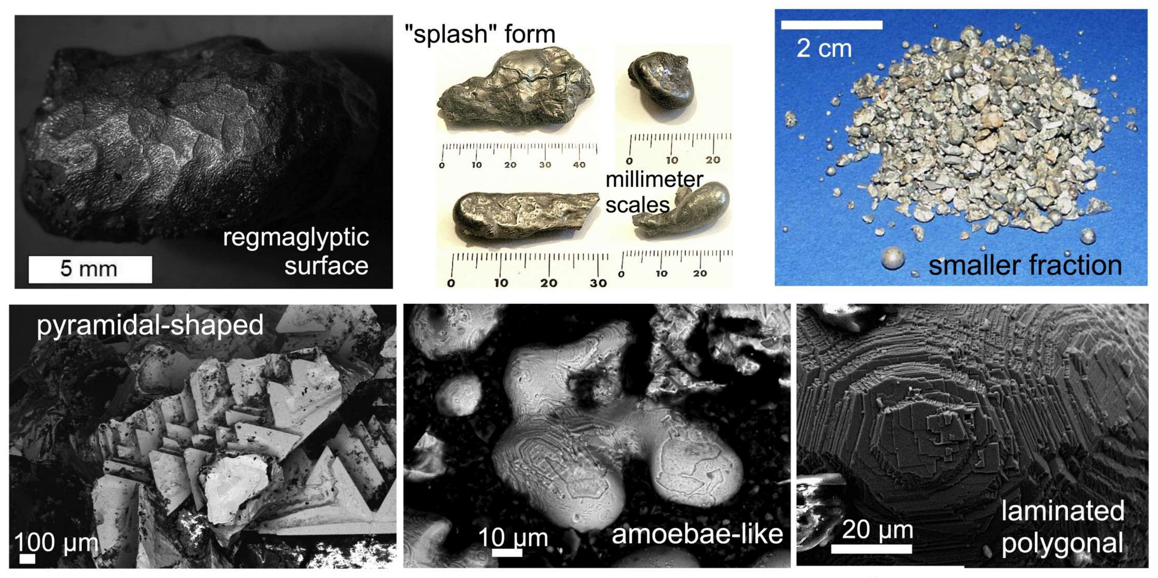
Location map for the Chiemgau impact crater strewn field and iron silicide occurrences.

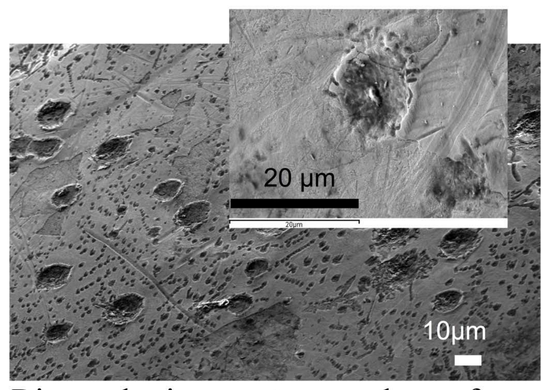
The eight kilograms iron silicide boulder from Grabenstätt. Centimeter scale.

The Chiemgau meteorite impact event and the enigmatic world of the external and internal structure of the iron silicides

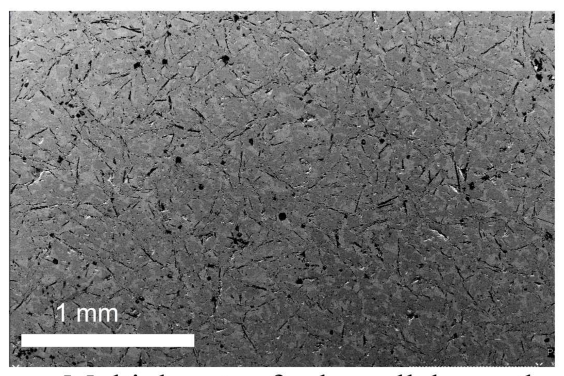
The discovery of the Chiemgau meteorite crater strewn field was directly paralleled by the abundant finds of iron silicides comprising gupeiite, xifengite, hapkeite, naquite and linzhite, and containing various carbides like, e.g., moissanite SiC, titanium carbide TiC and khamrabaevite (Ti,V,Fe)C, and calcium-aluminum-rich inclusions (CAI), minerals krotite and dicalcium dialuminate. 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.

Various aspects of the iron silicide finds from the Chiemgau impact strewn field

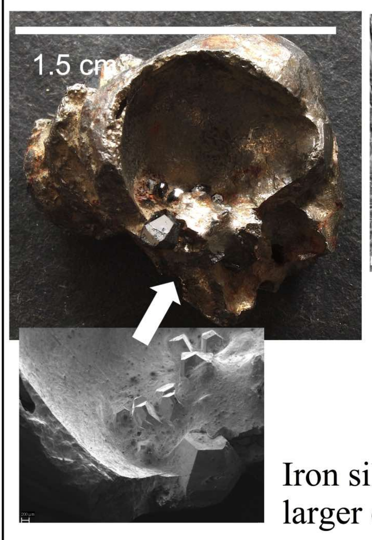


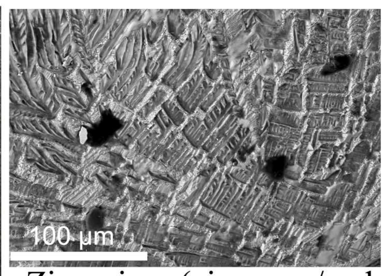


Rimmed micro-craters on the surface of an iron silicide piece - cosmic particle impacts?

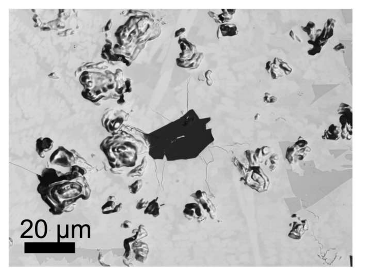


Multiple sets of subparallel, mostly open fractures in iron silicide matrix - shock spallation?





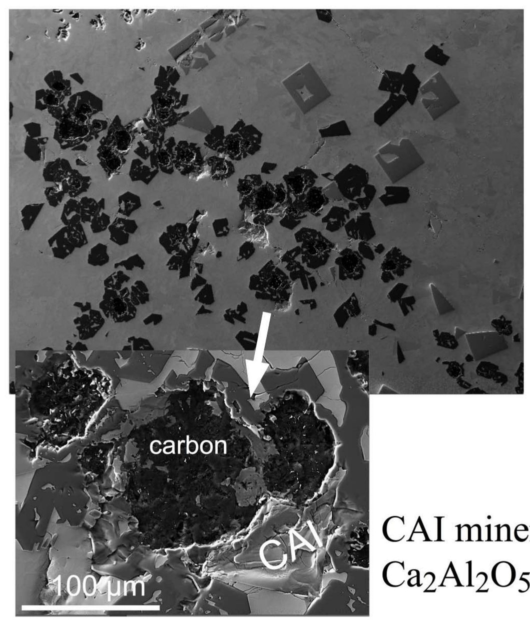
Zirconium (zircon or/and baddeleyite) possible exsolution lamellae in iron silicide.



Peculiar ornate structures in the iron silicide matrix. Possibly spotty melting of the matrix.

Iron silicide particle with sparkling silicon carbide (moissanite) larger crystals sticking out from the metallic matrix

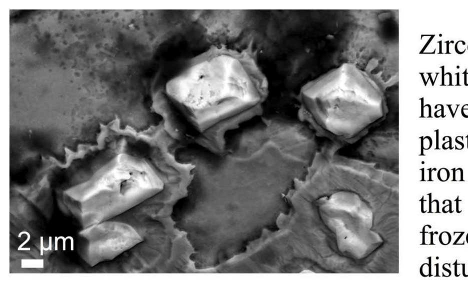
Iron silicides and the Chiemgau meteorite impact event - cont.: mineral inclusions - SEM, TEM and EBSD



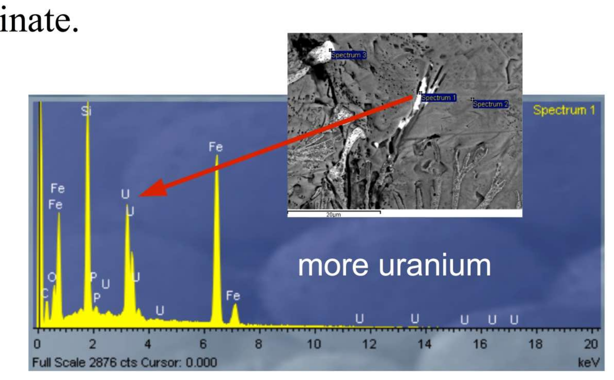
Typical texture of many iron silicide particles: titanium carbides TiC, khamrabaevite (Ti,V,Fe)C, $TiC_{0.63}$ off-stoichiometric (dark gray), silicon carbide (cubic moissanite SiC, black crystals) and CAI (whitish rims) in a matrix of intergrowth of various iron silicide minerals (gupeiite, xifengite, hapkeite, fersilicite, ferdisilicite, traces of suessite).

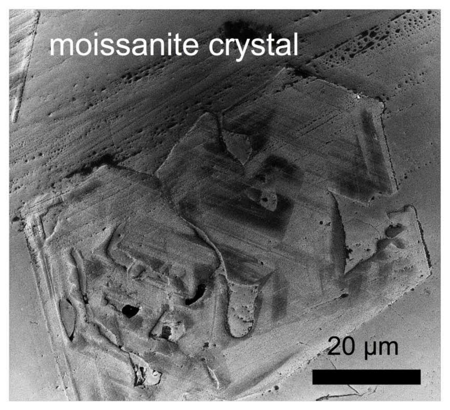
CAI minerals are $CaAl_2O_4$, calcium monoaluminate, krotite, and $Ca_2Al_2O_5$, dicalcium dialuminate.

zircon, uranium

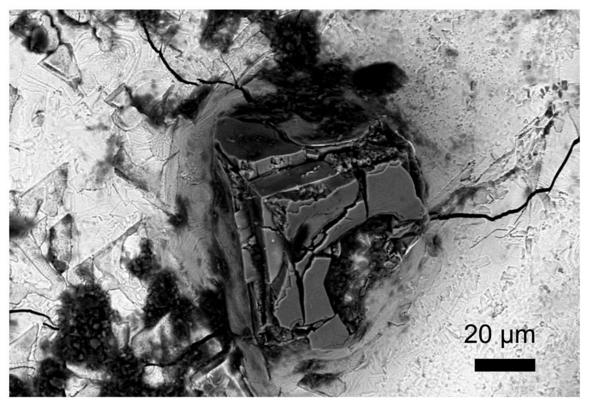


Zircon crystals with white uranium tips have impacted a plastic or liquid iron silicide matrix that seems to have frozen during the disturbance.





Multiple sets of planar features - probably a shock effect.



titanium carbide crystal strongly fractured

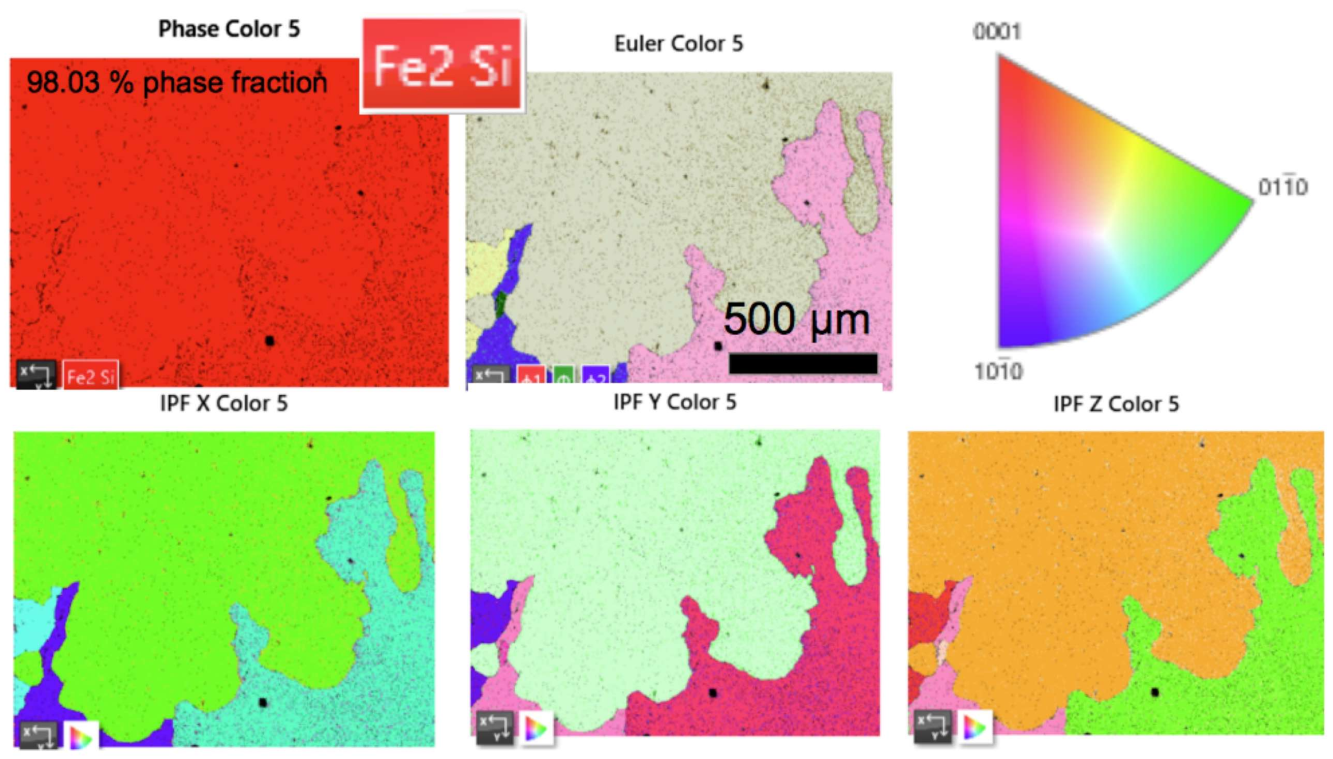
open, tensile fractures: dynamic shock spallation (?)

In addition to the main components Fe and Si, more than 30 other chemical elements, including uranium, the REE cerium, yttrium and ytterbium, or gallium, have been detected so far.

Hapkeite and the 8 kg iron silicide boulder from the Chiemgau impact strewn field

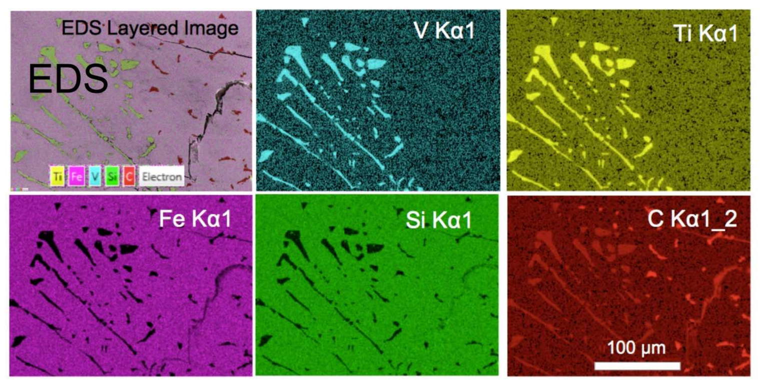
Method. - From the strongly magnetic boulder splinters of thumbnail size were removed and provided with mirror polish for SEM, TEM and EBSD analyses, and Raman spectroscopy.

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.

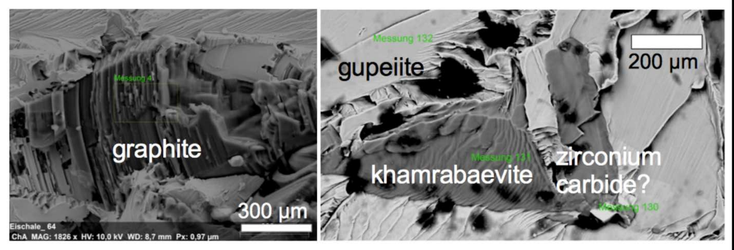


EBSD reveals nearly 100% Fe_2Si, hapkeite, with conspicuous grain boundaries.

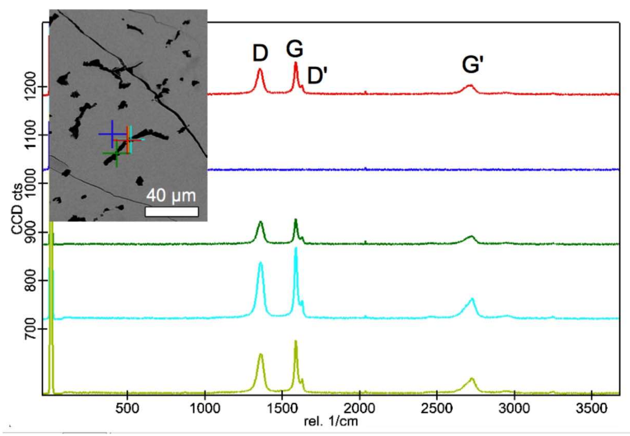
From the EBSD analyses of one boulder splinter (this fig.) the general texture proved to be Fe_2Si making the main mass (98,3 % phase fraction). The phase description for the Fe_2Si is the trigonal crystal system [7, 8]. The reniform contact of the four differently oriented grains far from any crystallographic 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.



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



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



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

At a second position of the 8 kg block, titanium carbide/khamrabaevite and carbon inclusions were established also in a matrix of cubic hapkeite and cubic gupeiite.

Discussion

- First artificial preparation of Fe_2Si (unclear polymorph) in 1939 [13].
- A trigonal (P3-m1), and a tetragonal (Pm3-m) Fe_2Si polymorph are described in [9-12].
- First detection of a cubic polymorph, hapkeite-1C in the lunar Dhofar 280 meteorite [14, 15], later also in a sample from the Luna 24 Mare Crisium landing site [16] and in an Apollo 16 regolith sample [17].
- Recently hapkeite (1–2 µm) 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].
- Fe_2Si 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 hapkeite polymorph – the most stable among the silicides (up to 255 GPa) – in conjunction with xifengite (Fe_5Si_3), gupeiite (Fe_3Si), and inclusions of cubic SiC (moissanite) and (Ti,V,Fe)C (khambraevite) superpure crystals, was discovered in a sample coming from the Chiemgau Impact area [3].

These findings show that Fe_2Si 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 Fe_2Si in a fulgurite [23] is mentioned for reasons of completeness. Only now Fe_2Si (all polymorphs) come into focus for industrial application.

Conclusions

➢ 8 kg boulder of massive iron silicide found in close proximity to the Lake Tüttensee meteorite crater in the Chiemgau impact strewn field contains hapkeite in cubic and trigonal phase.

➢ No artificial production, no fulgurite: the boulder is very probably of extraterrestrial origin.

➢ There is every evidence that the 8 kg boulder belongs to the family of the previously found iron silicides in the Chiemgau meteorite impact strewn field.

➢ It is the biggest sample known to contain natural Fe_2Si in its cubic phase (hapkeite-1C).

➢ The earlier reported companion trigonal Fe_2Si [3] is the first natural occurrence of that polymorph.

➢ For reasons of definiteness we suggest to name the trigonal Fe_2Si polymorph hapkeite-2T possibly rating a new mineral name.

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