

# CALCIUM-ALUMINUM-RICH INCLUSIONS (CAIs) IN IRON SILICIDE (XIFENGITE, GUPEIITE, HAPKEITE) MATTER: EVIDENCE OF A COSMIC ORIGIN

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## Abstract

Mm- to cm-sized metallic particles in the subsoil of the Alpine Foreland are composed of iron silicides Fe<sub>3</sub>Si, mineral gupeite, Fe<sub>5</sub>Si<sub>3</sub>, mineral xifengite, Fe<sub>2</sub>Si, mineral hapkeite, FeSi, fersilicite, and FeSi<sub>2</sub>, ferdilicite, the minerals gupeite, xifengite and fersilicite being the main components. More peculiar mineral components add to the matrix also hosting larger crystals of extremely pure titanium carbide, mineral khamrabaevite, and silicon carbide, mineral moissanite. Intriguing components are CAIs proved to be Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> (dicalcium aluminate) and the calcium aluminate CaAl<sub>2</sub>O<sub>4</sub>. This strange cocktail, evidence of shock effects, and last but not least the find situations of the particles speak in favor of a meteoritic origin of the iron silicide pieces and suggest a relation to the Holocene large Chiemgau impact event.



Fig. 1. Location map for the finds of the iron silicides.

## Introduction

- Iron silicides have been playing a major role in the discovery and discussion of the Holocene large Chiemgau meteorite impact event [1-15].
- They were detected by local history researchers in the Alpine Foreland (Southeast Germany, Fig. 1) in the subsoil down to the substratum.
- The iron silicides proved to be Fe<sub>3</sub>Si, mineral gupeite, and Fe<sub>5</sub>Si<sub>3</sub>, mineral xifengite. The iron silicides regularly occurred near rimmed craters.
- Early conclusion: Both the strange matter and the craters could perhaps be related with a meteorite impact in historical time, especially with regard to strongly restricted terrestrial formation of gupeite and xifengite and their occurrences in cosmogenic globular particles from the Yanshan area in China [16].
- An industrial origin was considered because the iron silicides had been produced in the local industry as a completely unknown byproduct.
- An industrial production could largely be excluded because of many find situations absolutely incompatible with anthropogenic support.
- Here, we report on completely new analyses of these iron silicide particles from different locations using various SEM and TEM techniques. They show the industrial hypothesis can be ruled out with a high degree of probability, and they suggest a cosmic, extraterrestrial origin.

## The material (Fig. 2)

- The mass of iron silicides so far sampled in the region totals roughly 2 kg.
- The size of the particles ranges between the order of a millimeter and a few centimeters. The largest piece is 6 cm long and has a mass of 162 g.
- Some of the particles exhibit a spherical or ellipsoidal shape, but often a convex smooth front combines with a flat irregularly shaped rear side.
- The surfaces show metallic luster and lack practically any corrosion.
- In many cases, a regmaglyptic surface resembling ablation features of meteorites is striking.
- Frequently, sparkling crystals can be seen with the naked eye to stick out from the metallic matrix.

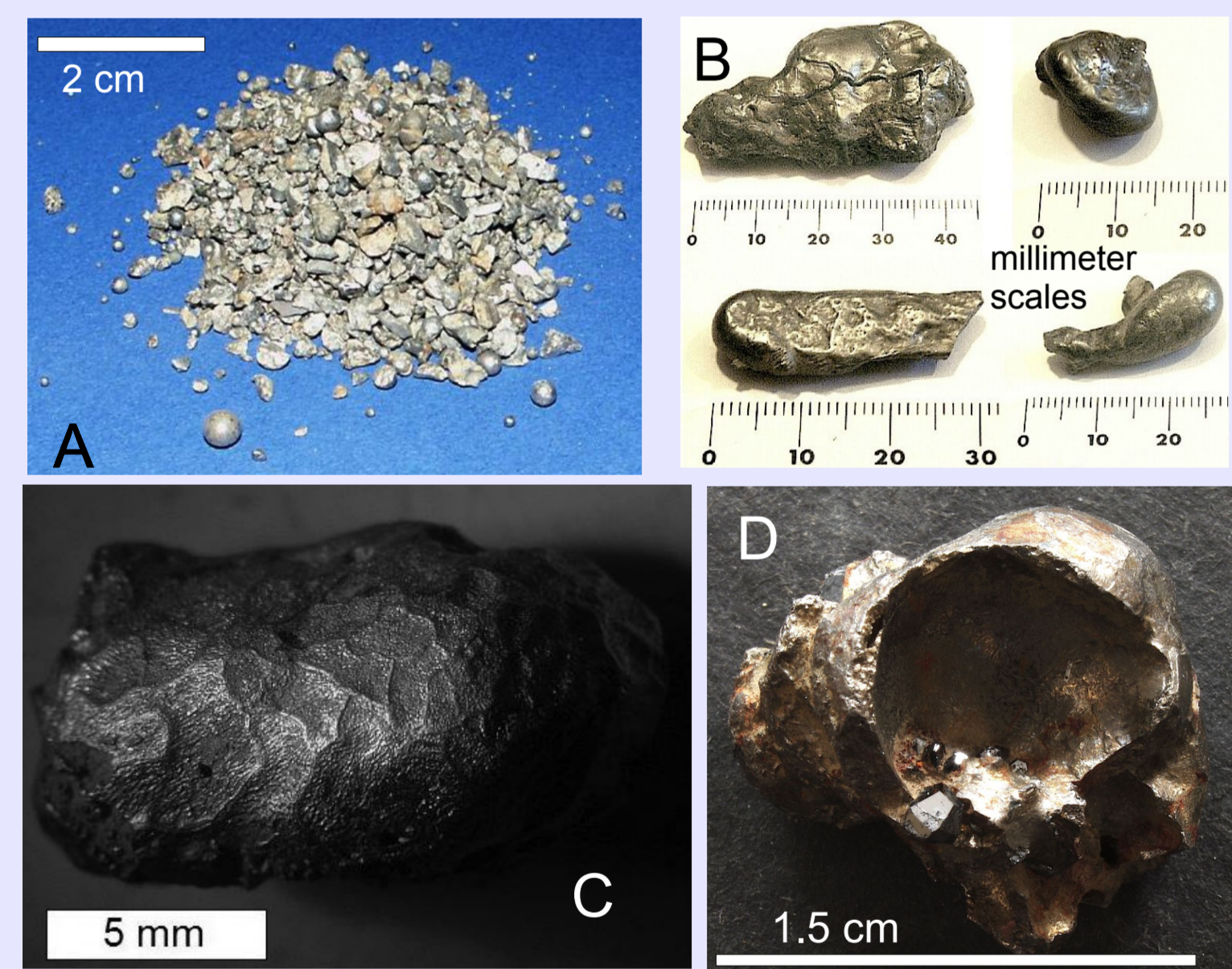


Fig. 2. The iron silicide matter from the Chiemgau region. A: small-sized metallic particles – angular and spherical. B: "Splash" form of iron silicide particles. C: Regmaglyptic surface of an iron silicide particle. D: Iron silicide particle with sparkling silicon carbide (moissanite) larger crystals sticking out from the metallic matrix.

## Analytical SEM, TEM and EBSD

Comprehensive SEM, TEM and EBSD analyses of 10 different iron silicide particles from the Chiemgau region have been performed and some hundred spectra were measured. More than 30 chemical elements (including, e.g., the REE cerium, neodymium and yttrium, but few nickel) have so far been established. The images on the whole show an enigmatic world of both the external and internal structure of the iron silicides an impression of which is given in the Figs. 3 - 18.

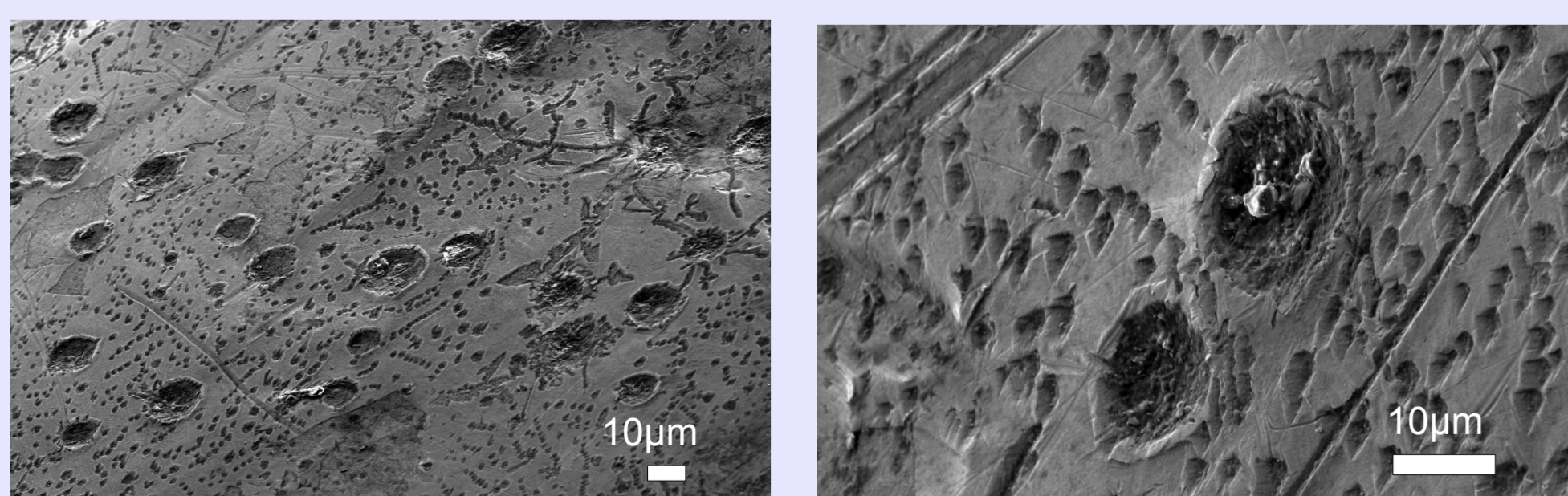


Fig. 3. Rimmed micro-craters on the surface of an iron silicide particle and two craters in more detail. The many angular pits could be imprints of zircon crystals now removed (see Fig. 5).

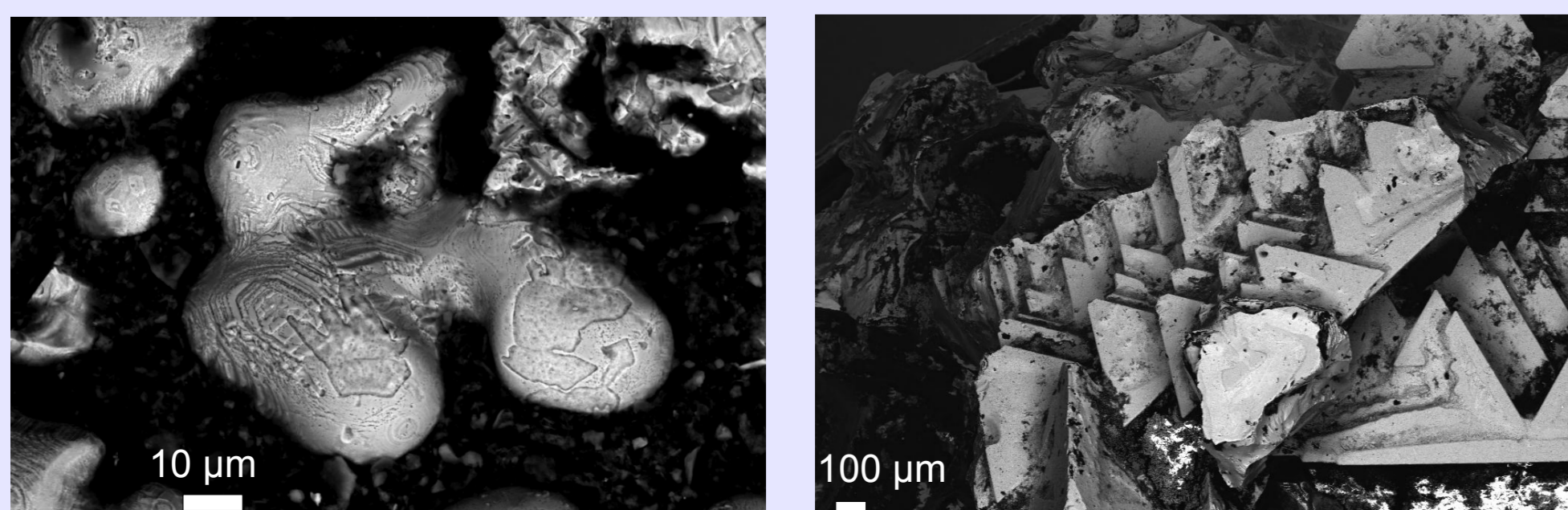


Fig. 4. Amoeba-like and pyramidal-shaped iron silicide in widely unstructured iron silicide.

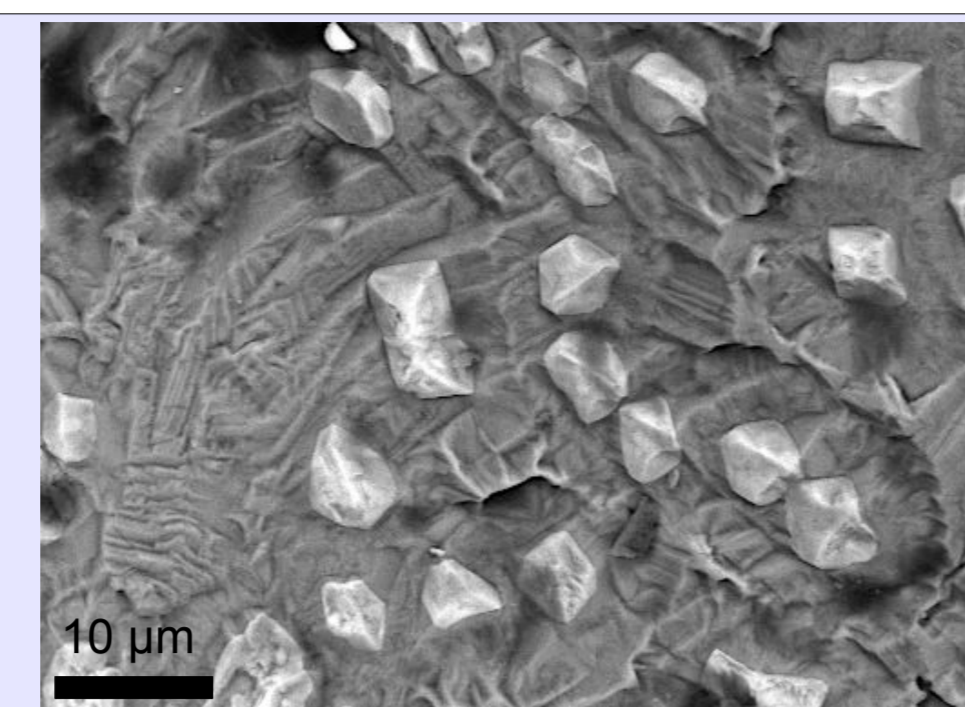


Fig. 5. Zircon crystals in iron silicide matrix. The white tips on the crystals have been shown to be uranium.

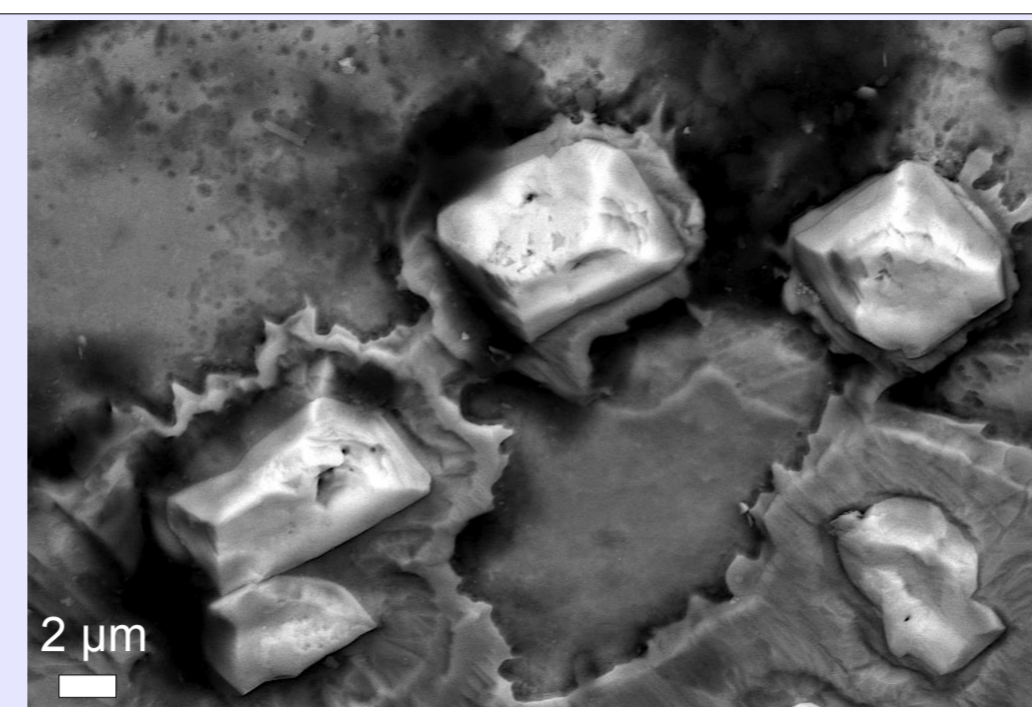


Fig. 6. Zircon crystals obviously having impacted a plastic or liquid iron silicide matrix that seems to have been frozen during the disturbance.

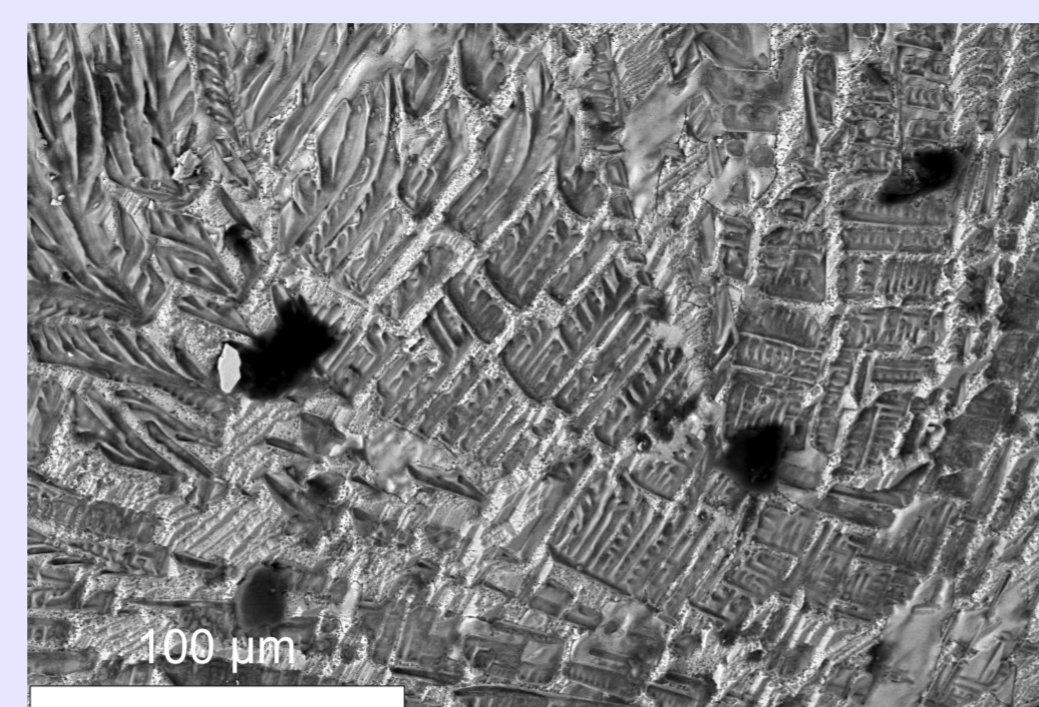


Fig. 7. Zirconium (zircon or/and baddeleyite) possible exsolution lamellae in iron silicide.

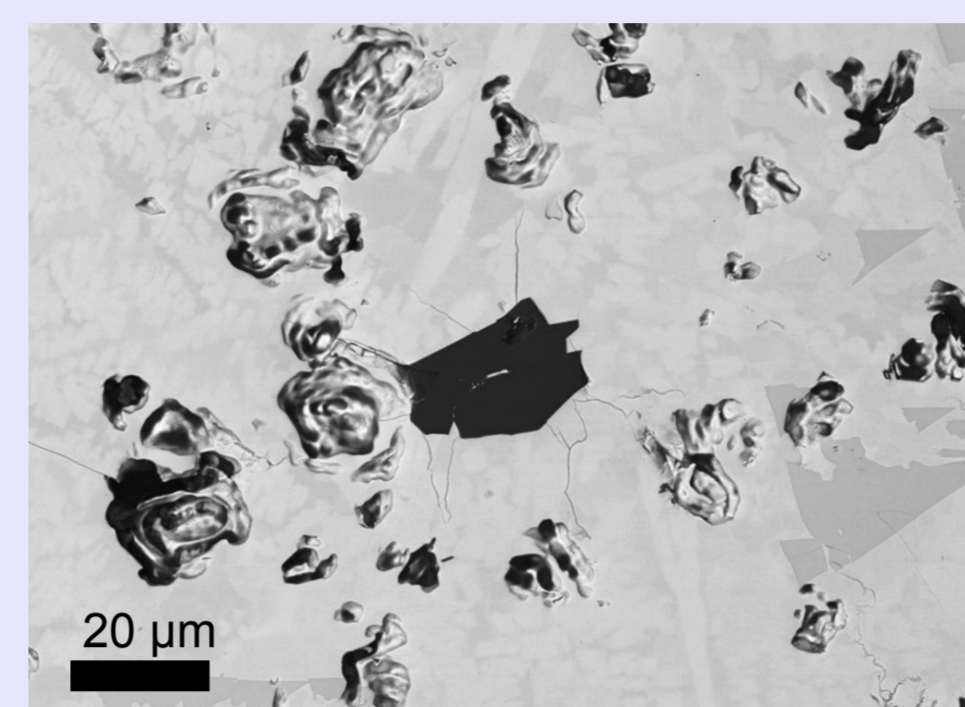


Fig. 8. Peculiar ornate structures in the iron silicide matrix lacking a conclusive explanation. Possibly spotty melting of the matrix.

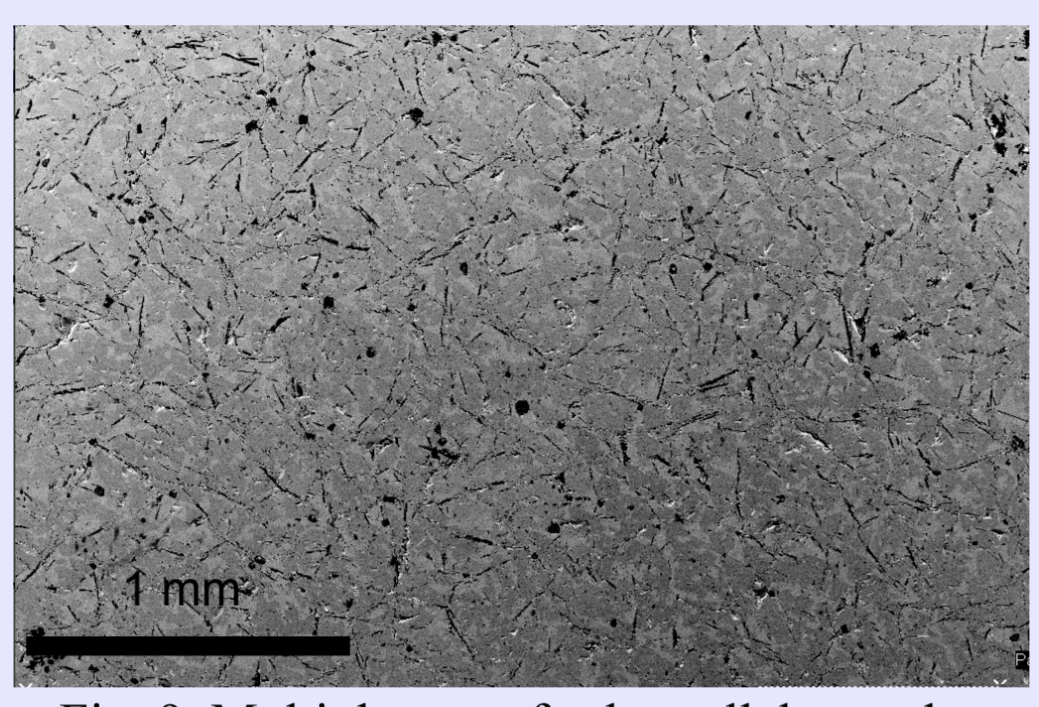


Fig. 9. Multiple sets of subparallel, mostly open fractures in iron silicide matrix.

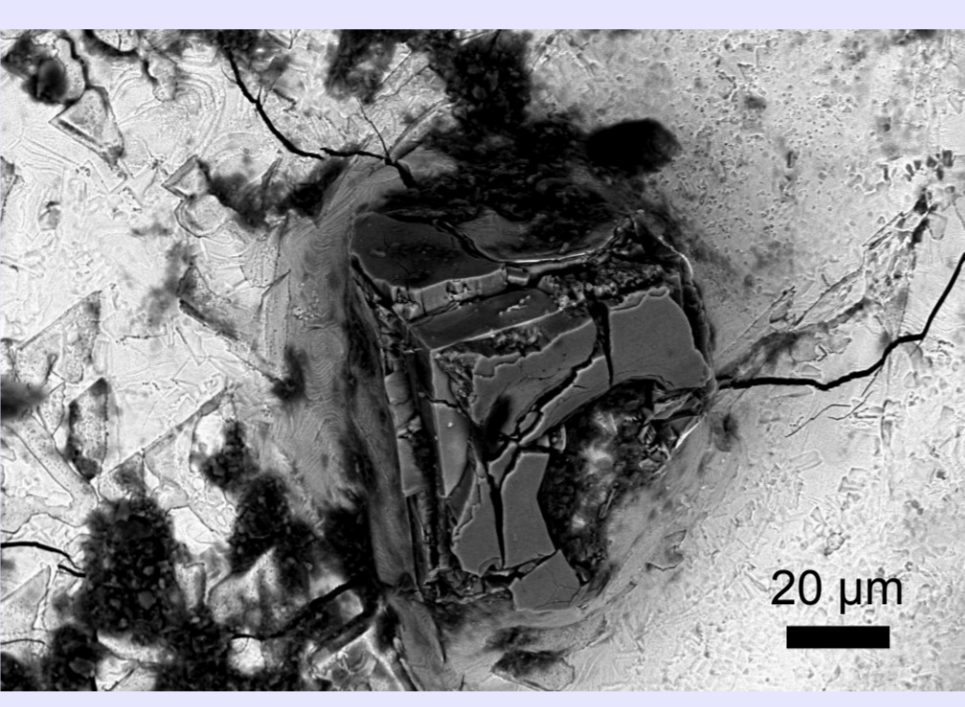


Fig. 10. Strongly fractured titanium carbide crystal in iron silicide matrix. Note the open, tensile fractures pointing to dynamic (shock?) spallation fracturing.

## Silicon and titanium carbides [SiC, moissanite, (Ti, V, Fe)C khamrabaevite]

- A significant feature of all analyzed iron silicide particles is their content of titanium and silicon carbides. They occur as extremely pure crystals and more finely dispersed in the matrix.
- The SiC has been analyzed to be the cubic moissanite mineral – (β)3C-SiC.
- The titanium carbide in general occurs as the (Ti, V, Fe)C mineral khamrabaevite, and also the off-stoichiometric form of TiC<sub>0.63</sub> has been shown to exist.
- Moissanite crystals may show multiple sets of planar features reminding of shock-produced planar deformation features (PDFs) known from various minerals.

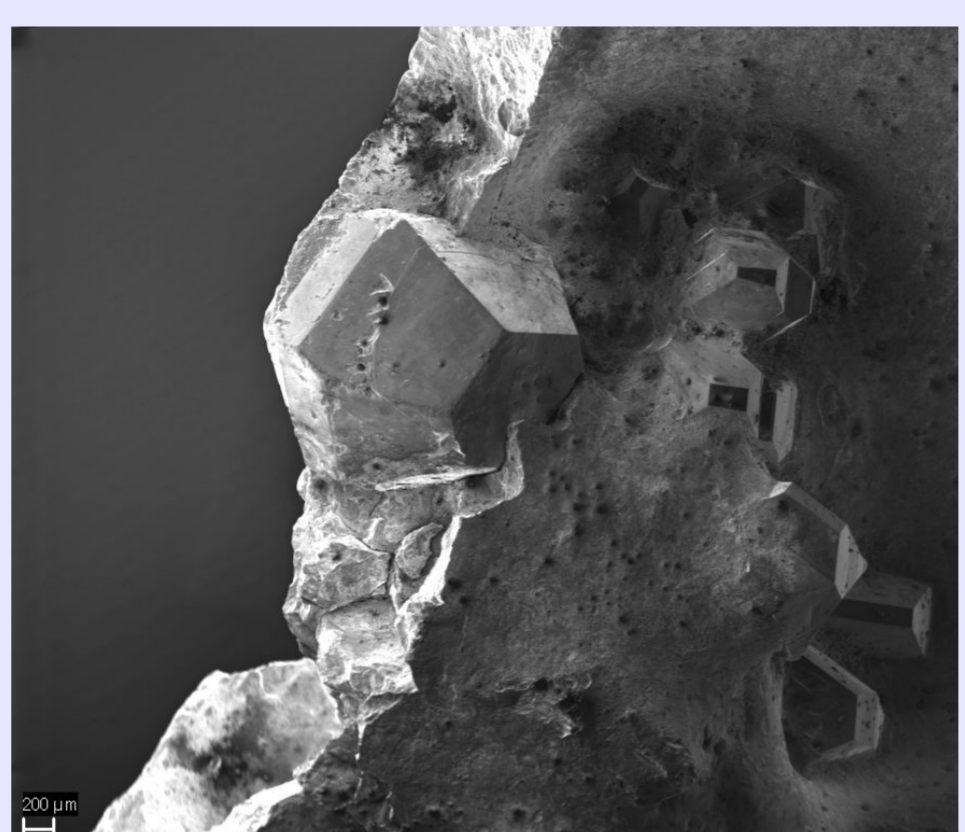


Fig. 11. Cubic moissanite crystals sticking out from the iron silicide matrix.

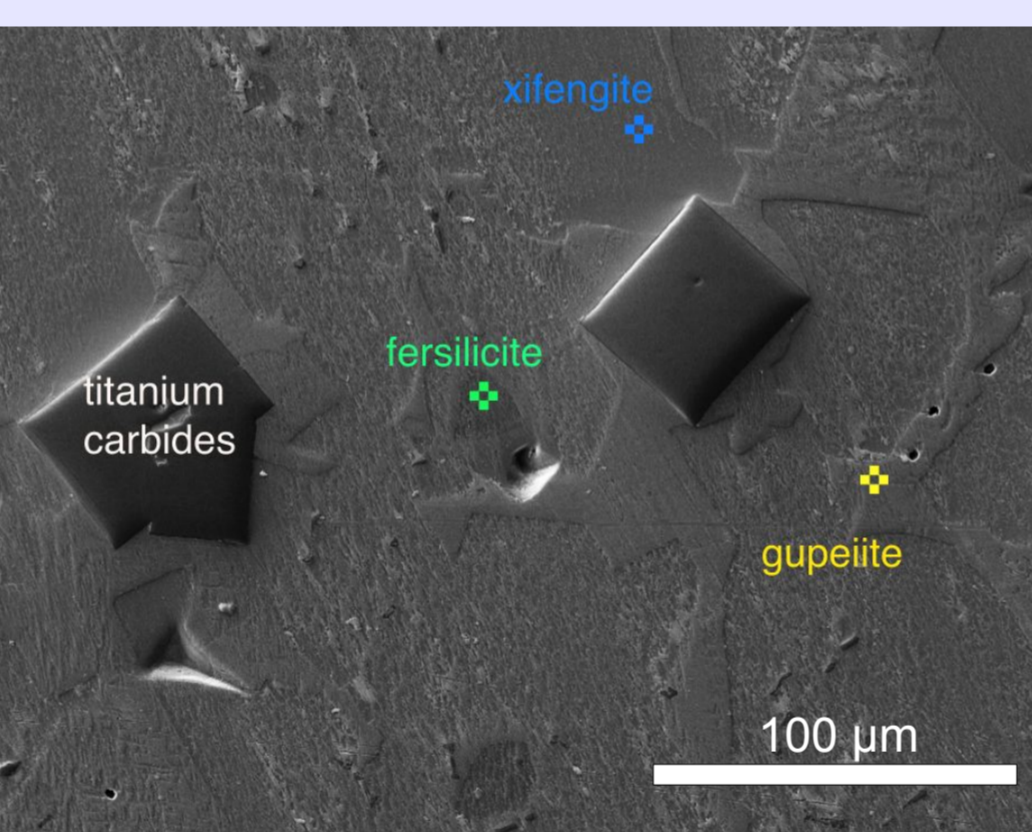


Fig. 12. Titanium carbide crystals in the matrix of intergrowth of FeSi, gupeite and xifengite iron silicides.

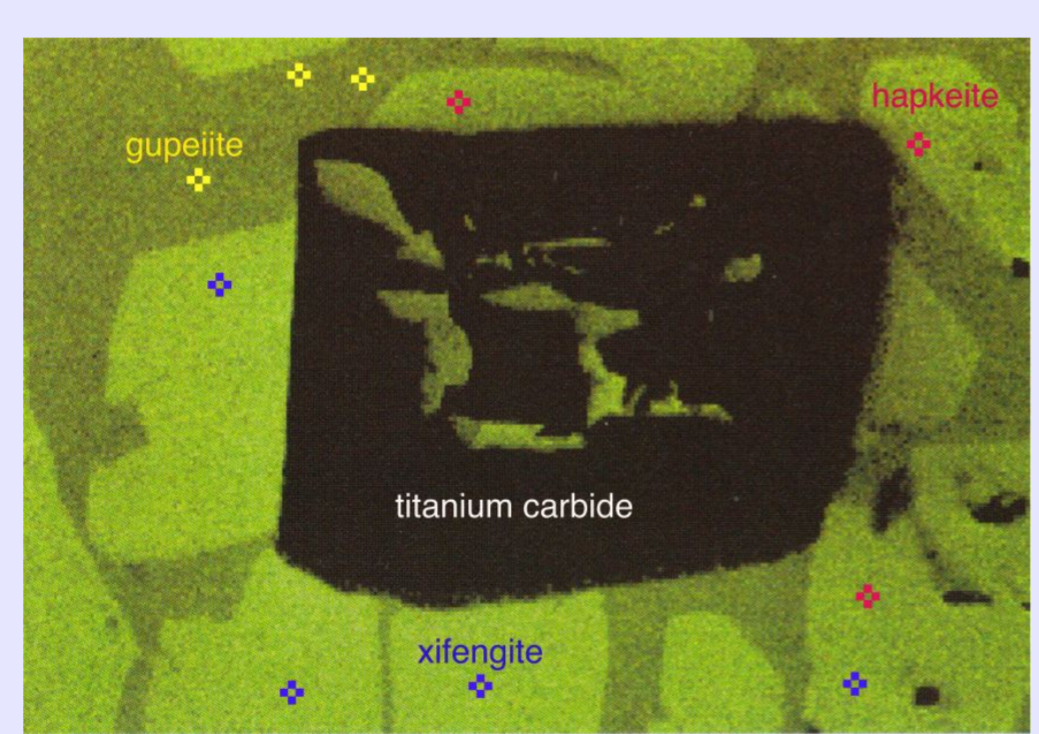


Fig. 13. Titanium crystal in the matrix of intergrowth of gupeite, hapkeite and xifengite iron silicides.

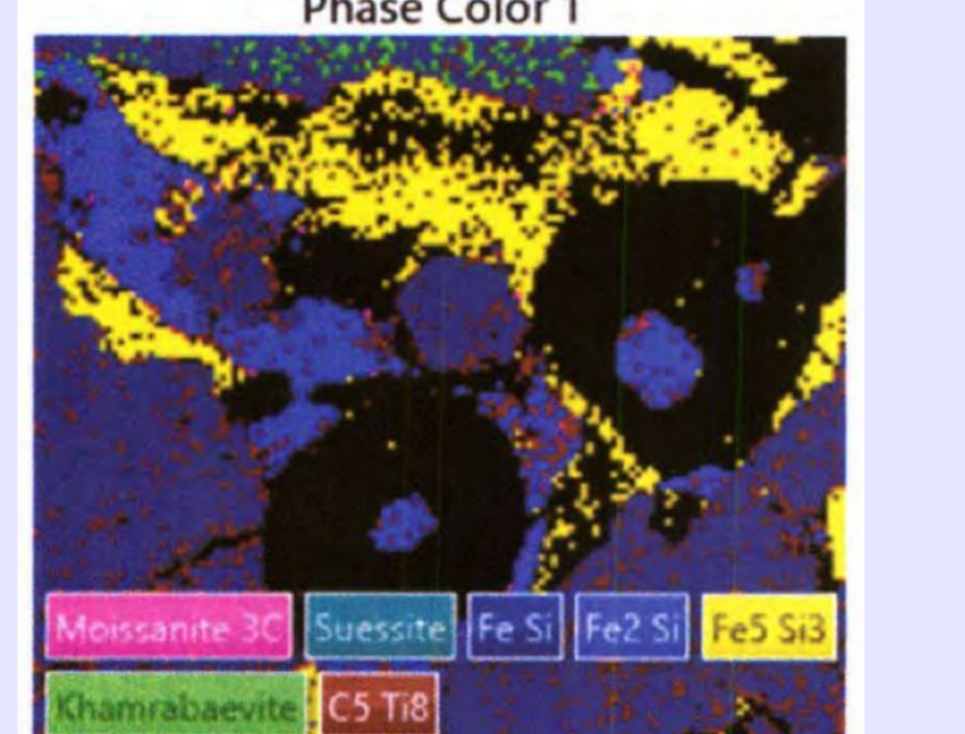


Fig. 14. Phase diagram for moissanite and titanium carbide phases in iron silicide matrix. Suessite is represented by only few counts. The black areas seem to be a calcium silicate near to wollastonite-1T without matching it and possibly being one of the several CaSiO<sub>3</sub> polymorphs.



Fig. 15. Multiple sets of planar features in a moissanite crystal - possibly a shock effect. Field width 80 μm.

## Uranium

- Uranium is in general associated with zirconium or without zirconium.
- Except for traces of thorium in one spectrum only no other decay products were analyzed. Not any lead was seen in the uranium spectra, and all other measured spectra (totaling some hundred) proved to be free of lead, too.

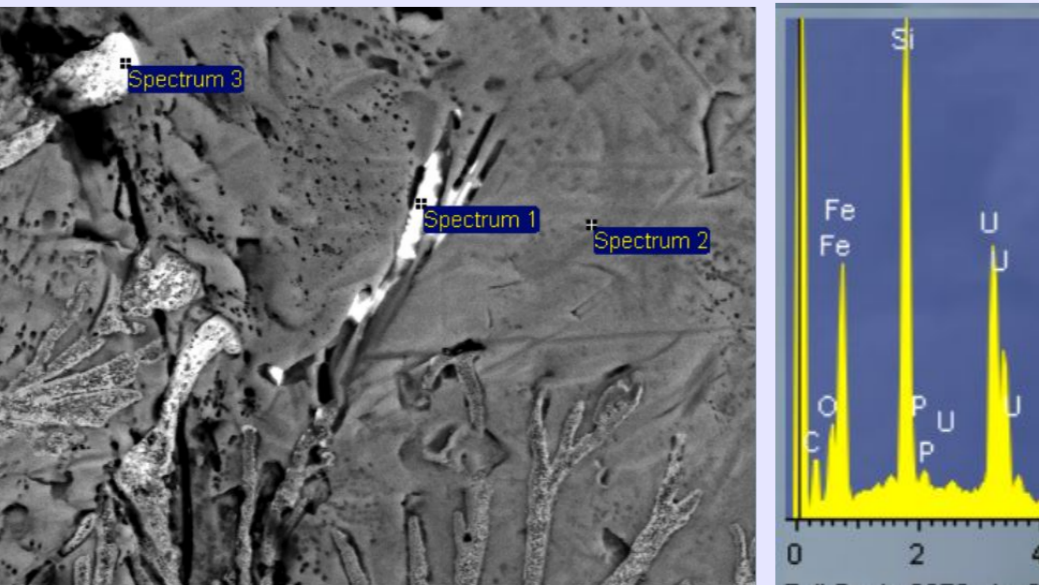


Fig. 16. Iron silicide with significant uranium peak in spectrum 1 (to the right). Spectrum 2 shows uranium and mostly zirconium (similar to Fig. 5), spectrum 3 more or less pure iron silicide. Spectra 2, 3 not shown here.

## The CAIs

- The iron silicides from the Chiemgau impact strewn field contain CAIs with minerals CaAl<sub>2</sub>O<sub>4</sub>, calcium monoaluminate, and Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub>, dicalcium dialuminate.
- The monoclinic high-temperature (>1,500°C), low-pressure dimorph of CaAl<sub>2</sub>O<sub>4</sub>, mineral krotite, was first identified in a CAI from the CH chondrite NWA 470 [17] and later reported [18, 19] to exist in a CAI in the carbonaceous chondrite meteorite NWA 1934.
- The orthorhombic Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> dicalcium dialuminate high pressure phase with the brownmillerite-type structure was established in 2000 [20] and has so far no natural counterpart. Experimental data were 1,250°C and 2.5 GPa, and stability was reached between 4 and 9 GPa and at ≈ 1,500 K.

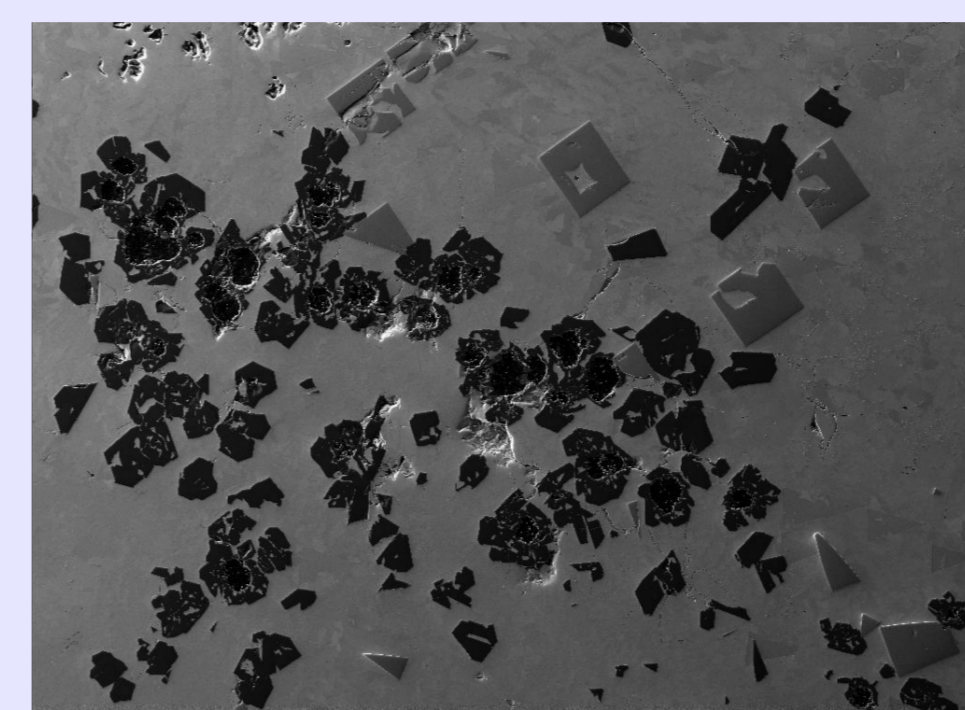


Fig. 17. The CAIs (stronger magnification in Fig. 18) have been established in this typical texture of many iron silicide particles: titanium carbide (dark gray) and silicon carbide (moissanite, black) crystals in a matrix of intergrowth of various iron silicide minerals (gupeite, xifengite, hapkeite, fersilicite, ferdilicite).

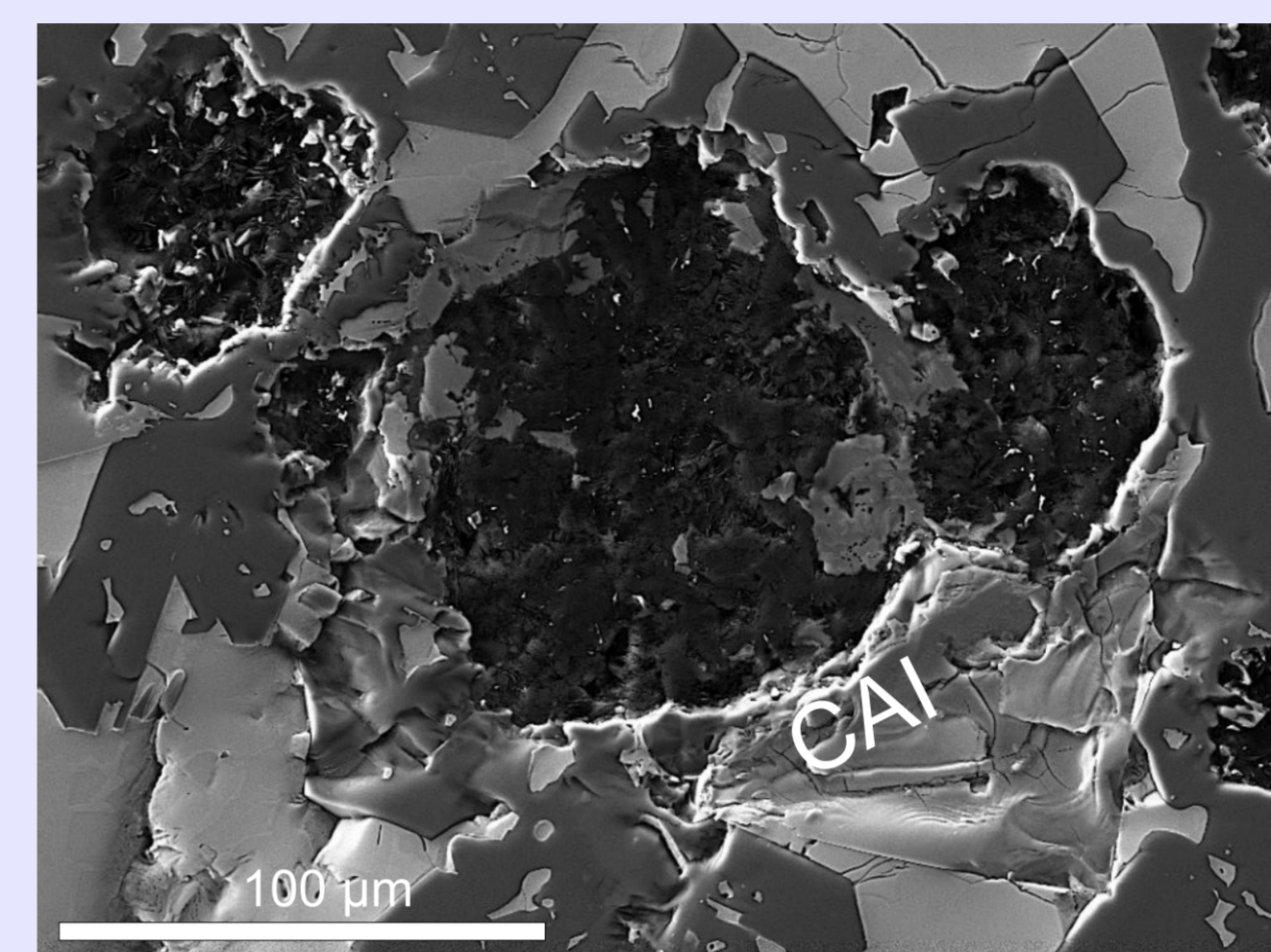


Fig. 18. Iron silicide matrix (light gray) with inclusions of TiC (dark gray), moissanite SiC with black C (graphite, diamond?) film and light edging CAIs.

## Discussion and relations

### The Chiemgau impact and meteorite crater strewn field

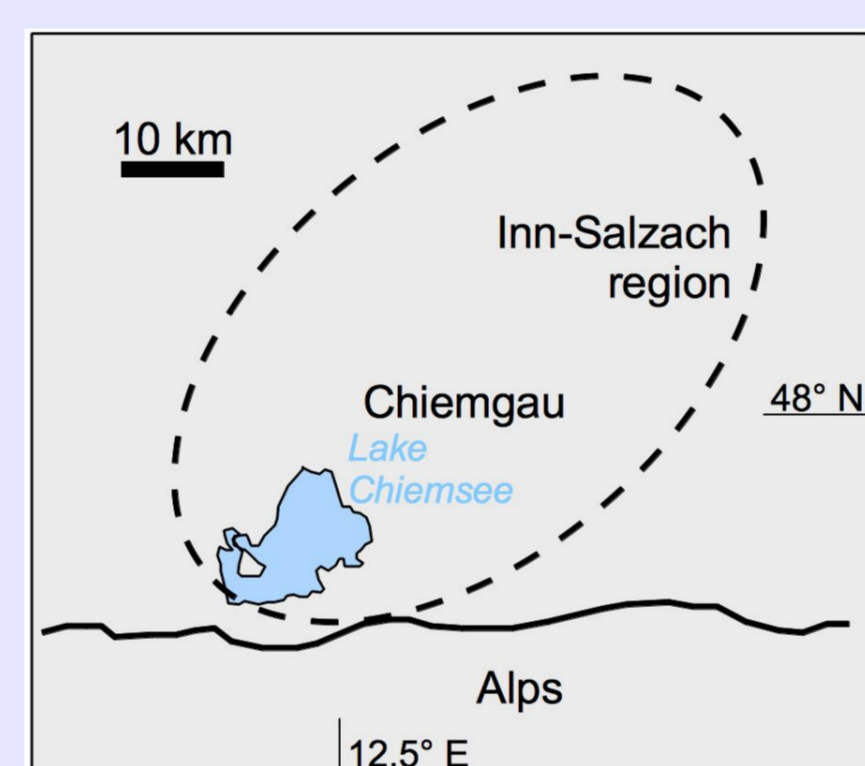


Fig. 16. Location map of the Chiemgau impact elliptically shaped strewn field (see Fig. 1).

- The Chiemgau strewn field [3, and references therein] comprises more than 80 mostly rimmed craters scattered in a region of about 60 km length and ca. 30 km width in the very South-East of Germany (Fig. 16, Fig. 1).
- The crater diameters range between a few meters and a few hundred meters, among them Lake Tüttensee, the hitherto established largest crater of the strewn field with a rim-to-rim diameter of about 600 m and an extensive ejecta blanket.
- Geologically, the craters occur in Pleistocene moraine and fluvio-glacial sediments.

- The impact is substantiated by [3, and references therein]
  - ▶ heavy deformations of the Quaternary cobbles and boulders in and around the craters
  - ▶ abundant fused rock material (impact melt rocks and various glasses) occur.
  - ▶ shock-metamorphic effects (planar deformation features, PDFs, diaplectic glass)
  - ▶ geophysical anomalies
  - ▶ abundant occurrence of metallic, glass and carbon spherules, accretionary lapilli
  - ▶ high-pressure/high-temperature carbon allotropes [7, 13].
- The impactor is suggested to have been a roughly 1,000 m sized low-density disintegrated, loosely bound asteroid or a disintegrated comet in order to account for the extensive strewn field.

### The Chiemgau impact and the iron silicides

There is strong evidence that the iron silicides are linked to the Chiemgau meteorite impact event:

- Many find situations in the Chiemgau area are practically excluding any anthropogenic deposition.
- There is an obvious extraterrestrial relation of most other gupeite and xifengite iron silicide occurrences on earth.
- There is a problematic formation of gupeite and xifengite in a geologic oxygen-free environment.
- Tiny iron silicide particles are frequently incorporated in accretionary lapilli from the Chiemgau strewn field.
- Iron silicide particles are interspersing highly porous carbonate recrystallization relics of probably carbonate impact melt.
- "Splash" forms and regmaglyptic surfaces (Fig. 2) point to aerodynamic processes.
- There is evidence of one or more shock events the iron silicides underwent:
  - ▶ Moissanite crystals in part show multiple sets of closely spaced planar features (Fig. 15) reminding of shock-produced planar deformation features (PDFs) known from various minerals.
  - ▶ The peculiar occurrence of uranium without its decay products (Fig. 16) may be interpreted as the result of a shock event that could have led to complete resetting of the U-Pb isotopic system as is observed e.g., in some tektites [21] and in zircons from the Chicxulub K-T impact event [22].
  - ▶ Ubiquitous open fractures traversing the iron silicide particles in irregular patterns (Fig. 10) and as multiple sets of subparallel open fissures (Fig. 9) are implying tensile character of the deformations and may easily be explained by impact shock spallation.
  - ▶ The occurrence of the many micrometer-sized rimmed craters on the surface of an iron silicide particle (Fig. 3) may point to a highly energetic cosmic bombardment, and the supposed open imprints of lost zircon crystals (Fig. 3) could possibly be witness of a shock collision in space.
  - ▶ The impact of tiny zircons into a plastic or even liquid matter and the obvious sudden freezing of the expansion waves of the disturbance (Fig. 6) point to abrupt change of the material's properties.

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## The CAI cosmic relevance

Opponents and critics of the Chiemgau impact *per se* don't grow tired of pointing to an industrial byproduct of the iron silicides [23]. They ignore:

- Iron silicides occur in the most reduced meteorites.
- Cubic moissanite and titanium carbide exist in some meteorites and have been verified in cosmic dust.
- On earth, the hapkeite, Fe<sub>2</sub>Si iron silicide (in its cubic form) is known from the Dhofar 280 lunar fragmental breccia meteorite [24] and has been reported for magnetic spherules in Hungary that are ascribed to cosmic dust or meteorite impact [25]. A grain similar in composition to hapkeite occurs in the FRO 90228 ureilite [26], and Fe<sub>2</sub>Si, together with TiC and supernova material, was established in the Orgueil meteorite [27].

Now, apart from the strong evidence for shock processes, the established CAIs add to the cosmic component of the Chiemgau iron silicides. CAIs are a mineralogically and chemically diverse group of structures mainly known from carbonaceous chondrites. They consist of various minerals that formed from a high temperature gas at early stages of the Solar System formations.

For the krotite the conditions of high temperature and low pressure are consistent with a hypothesis that the mineral found in the NWA 1934 meteorite formed as high-temperature condensate from the solar nebula.

## Conclusions

For the iron silicide particles the intimate CAI coexistence of the high-temperature/low-pressure CaAl<sub>2</sub>O<sub>4</sub> krotite and the high-pressure Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> phase imply a complex formation history. In addition to the many other peculiar properties (xifengite, gupeite, hapkeite, fersilicite, ferdilicite intergrowth, extremely pure, in part larger crystals of cubic moissanite and khamrabaevite, various indications of probable shock effects) featured by the iron silicides from the Chiemgau meteorite impact strewn field, the CAIs substantiate an extraterrestrial origin of these metallic particles.

For the time being the general question remains unanswered whether the proposed shock was experienced during a cosmic passage of the iron silicides or in the terrestrial event of the Chiemgau impact.

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