# Meteorite impact on a micrometer scale: iron silicide, carbide and CAI minerals from the Chiemgau impact event (Germany)

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# Introduction



The Holocene Chiemgau impact event is considered to have produced a large meteorite crater strewn field in southeast Bavaria, Germany ([1-14], Fig. 1). The impact is documented by abundant impact melt rocks and various glasses, shock-metamorphic effects like planar deformation features (PDFs) and diaplectic glass, geophysical anomalies and ejecta deposits, and substantiated by the abundant occurrence of metallic, glass and carbon spherules. Microtektites [14] and accretionary lapilli add to the impact signature. Enigmatic carbon matter containing carbynes and diamond-like/carbyne-like carbon allotropes also testify extreme temperatures and pressures [7, 11]. From dating archeological objects the impact must have happened more than 2500 years BP in the Bronze Age/Celtic era. From the beginning of the discovery and investigation of the strewn field comprising craters sized between a few meters and a few hundred meters, extended finds of iron silicide particles in the subsoil mainly composed of xifengite and gupeiite and obviously associated with the craters played a significant role as possible meteoritic matter. New analytical SEM, TEM and EBSD have shown that the iron silicides when going down to micrometer scales are hosting a real "zoo" of more than 30 chemical elements, extremely rare minerals and peculiar textural features.

Fig. 1. Location map for the Chiemgau meteorite crater strewn field.

# **Observations and analyses**

#### Iron silicides

The mass of iron silicides (Fig. 2 A) so far sampled in a region of roughly 60 km x 30 km totals about 2 kg. The size of the particles ranges between the order of a millimeter and few centimeters. The largest piece is 6 cm long and has a mass of 162 g. The surfaces show metallic luster and lack practically any corrosion. In many cases, a regmaglyptic surface resembling ablation features of meteorites is striking (Fig. 2 B), and splash forms and spherules are common (Fig. 2 C, A). Frequently, sparkling crystals can be seen with the naked eye to stick out from

# Carbides (silicon carbide - moissanite, titanium carbide, khamrabaevite)

A significant feature of all analyzed iron silicide particles is their content of titanium and silicon carbides. They occur as extremely pure crystals (Fig. 2, Fig. 5) and more finely dispersed in the matrix (Fig. 3). The SiC has been analyzed to be the cubic moissanite mineral  $-(\beta)3C$ -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 (Fig. 3).



Fig. 5. A: Titanium carbide/khamrabaevite (Ti,V,Fe)C; dark gray) and silicon carbide (moissanite, SiC; black) crystals in a matrix of intergrowth of xifengite, gupeiite and fersilicite. B: Tightly packed titanium/khamrabaevite crystals in iron silicide matrix. C: SEM image of cubic moissanite crystals sticking out from the iron silicide matrix. D, E: EDX spectrum and electron back scatter diffraction of moissanite from the Chiemgau strewn field. Images: Carl Zeiss microscopy and

the metallic matrix (Fig. 2 D).



Fig. 2. Various aspects of the the iron silicide particles from the Chiemgau impact strewn field (see text). Images: CIRT

#### Matrix

So far the iron silicide minerals gupeiite (Fe<sub>2</sub>Si), xifengite (Fe<sub>5</sub>Si<sub>2</sub>), fersilicite (FeSi), ferdisilicite (FeSi<sub>2</sub>) and hapkeite (Fe<sub>2</sub>Si) have been analyzed while gupeiite, xifengite and fersilicite are constituting the main mass of the particle matrix.







Fig. 3. EBSD: various aspects of the iron silicide matrix exhibiting a complex texture. To the left: red = fersilicite, green = ferdisilicite, yellow = gupeiite, margenta = xifengite as the principal phases. To the right: Suessite is represented by only few counts. The black areas seem to be a calcium silicate near to wollastonite-1T. For the carbide mineral inclusion see the the extra chapter. Images: Carl Zeiss microscopy and Oxford Instruments.

**Oxford Instruments.** 

#### CAIs - calcium aluminum inclusions

Recent analyses [17] have shown that the 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 [18] and later reported [19, 20] to exist in a CAI in the carbonaceous chondrite meteorite NWA 1934. orthorhombic



Ca<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> dicalcium dialumiate high pressure phase with the brownmillerite-type structure was established in 2000 [21] 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  $\approx 1,500$  K.

Fig. 6. Iron silicide matrix (light gray) with inclusions of TiC/(Ti,V,Fe)C and moissanite SiC (dark gray), and black spots of C (graphite, diamond, amorphous carbon?) film and light edging CAIs. Images: Carl Zeiss microscopy and Oxford Instruments.

**Deformation features** 







20 µm

Fig. 7. Iron silicide particles from the Chiemgau strewn field show in general a strong mechanical overprint. We observe open fractures in irregular patterns (Fig. 7 A) and as multiple sets of subparallel open fissures pointing to tensile deformation (B). These deformations and also the strongly fractured TiC crystal (C) suggest dynamic fracturing by shock spallation. Moissanite crystals in part show multiple sets of closely spaced planar features (D) reminding of shock-produced planar deformation features (PDFs) known from various minerals. E, F: The occurrence of the many micrometer-sized rimmed craters on the surface of an iron silicide particle may point to a highly energetic cosmic bombardment, and the supposed open imprints of lost zircon crystals could possibly be witness of a shock collision in space. Images: Carl Zeiss microscopy.

From the new SEM, TEM and EBSD investigations the existence of the iron silicide  $Fe_2Si$ , mineral hapkeite became evident as a very important mineral contributing to the Chiemgau iron silicides. In Fig. 2 (middle) hapkeite shows intergrown with gupeiite and xifengite to form the iron silicide matrix that is hosting a titanium carbide (TiC) crystal. In Fig. 2 (right) the Fe<sub>2</sub>Si phase is also clearly documented and in part appears like the yolk of fried eggs within a so far unidentified calcium silicate phase, possibly a wollastonite polymorph. In the literature two hapkeite polymorphs, a cubic and a trigonal modification, have been reported, and here the trigonal polymorph (S.G. P3m1, No. 164 [15,16]) has been established.

### Internal structure and composition











# **Summary and Discussion**

In the beginning of the investigation of the Chiemgau iron silicides, relatively rough and cursory analyses found a simple intergrowth of xifengite, gupeiite, fercilicite and titanium carbide, left it at that and even suggested an industrial origin [24] despite the in most cases very peculiar find situations. The sophisticated new analyses we were now able to perform with the state-of-theart equipment are telling an entirely different story, in particular when we are looking down to micrometer and even nanometer scales. We state in note form:

- iron silicide minerals gupeiite, xifengite, fersilicite, ferdisilicite, hapkeite and stoichiometrically similar variants; traces of the meteoritic mineral suessite; the Chiemgau hapkeite is the trigonal polymorph (S.G. P3m1, No. 164 [15, 16]).
- + more than 30 chemical elements so far established (including the REE cerium, neodymium, yttrium; few nickel). Uranium is fairly common, frequently associated with zirconium minerals and cerium/neodymium; no uranium decay products including lead exist (except for two EDX spectra showing traces of thorium and polonium, respectively).
- + extremely pure crystals of titanium carbide (TiC, (Ti,V,Fe)C, khamrabaevite) and silicon carbide (SiC, moissanite) interspersing the iron silicide matrix.
- CAIs (calcium aluminum inclusions) in coexistence of the monoclinic high-temperature (>1,500°C), low-pressure dimorph of CaAl2O4, mineral krotite, and the orthorhombic Ca2Al2O5 dicalcium dialuminate high pressure phase pointing to complex formation conditions.
- probably one or more shock events the iron silicides underwent:
- moissanite showing multiple sets of closely spaced planar features (Fig. 7 D) very similar to shock PDFs
- uranium without its decay products (Fig. 4 G-I) interpreted as the result of a shock event that could have led to complete resetting of the U-Pb isotopic system (see, e.g., [22, 23]).
- ubiquitous tensile open fractures traversing the iron silicide particles in irregular patterns (Fig. 10) and as multiple sets of subparallel open fissures (Fig. 9) interpreted by impact shock spallation.

• clusters of micrometer-sized rimmed craters on the surface of an iron silicide particle (Fig. 3) interpreted by a highly energetic cosmic bombardment. The supposed open imprints of lost zircon crystals (Fig. 3) could possibly be witness of a shock collision in space.

• impact of tiny zircons into a plastic or even liquid matter and the obvious sudden freezing of the expansion waves of the disturbance (Fig. 4 J) pointing to abrupt change of the material's properties.





microscopy.



Fig. 4. Selected SEM images of multi-variant composition of the iron silicide particles. In fact, the aspects shown here are giving only a strongly limited insight into the immense diversity of textures and components. A, B: Amoebae-like and pyramidal-shaped iron silicide in widely unstructured iron silicide. C: Iron silicide possibly with beginning (and then stopped) secession of spheroidal melt particles. D: Spheroidal iron silicide particle with strange crystal form. E: Peculiar ornate structures in the iron silicide matrix lacking a conclusive explanation. Possibly spotty melting of the matrix. F: Zirconium (zircon or/and baddeleyite) possible exsolution lamellae in iron silicide. G: Zircon crystals in iron silicide matrix. The white tips on the crystals have been shown to be uranium. H: More uranium, here forming the whitish rim of zirconium inclusions I: Iron silicide with significant uranium peak in spectrum #1. Spectrum #2 shows uranium and mostly zirconium (similar to H), spectrum 3 more or less pure iron silicide. J: Zircon crystals obviously having impacted a plastic or liquid iron silicide matrix that seems to have been frozen during the disturbance. Images: Carl Zeiss

# Conclusions

Apart from the many peculiar properties (the xifengite, gupeiite, hapkeite, fersilicite, ferdisilicite 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 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 in particular substantiate an extraterrestrial origin of these metallic particles pointing at the same time to a possibly strange impactor to have produced the Chiemgau strewn field. Hence, we should get rid off the simple idea that impacts on earth are related with either stony or iron meteorites.

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.

#### References

1] Schüssler U. et al. (2005), Eur. J. Mineral. 2005, 17, Beih. 1, 124. [2] Rappenglück, M. et al. (2005) European J. of Mineralogy, 17, Bh 1, 108. [3] Ernstson, K. et al. (2010), J. Siberian Federal Univ., Engineering & Technology, 2010, 3/1, 72-103. [4] Hiltl, M. et al. 2011. Abstract #1391. 42nd Lunar & Planetary Science Conference. [5] Ernstson, K. & Rappenglück, M.A. (2008), International Scientific Conference "100 years of the Tunguska event". June 30-July 6, 2008, Krasnoyarsk (Russia). [6] Ernstson, K. et al. (2011), Cent. Eur. J. Geosci., 3(4), 385-397. [7] Isaenko, S. et al. (2012), Eur. Min. Conf., Vol 1, EMC 2012-217. [8] Ernstson, K. et al. (2013), Yushkin Memorial Seminar 2013, Proceedings, Syktyvkar: IG Komi SC UB RAS, 546 p. [9] Liritzis, I. et al. (2010), Mediterranean Archaeology and Archaeometry, 10, 17-33. [10] Rappenglück, M.A. & Ernstson, K. (2008), International Conference "100 years since Tunguska phenomenon: June 26–28, 2008, Moscow (Russia). [11] Shumilova T. G. et al. (2012), 43nd Lunar and Planetary Science Conference (2012), 1430.pdf. [12] Rappenglück, B. et al. (2012), 34th International Geological Congress, 5-10 August 2012, Brisbane.[13] Neumair, A. & Ernstson, K. (2011), Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec., GP11A-1023. [14] Ernstson, K. et al. (2014), 45th Lunar and Planetary science Conference (2014), 1200.pdf. [15] NIST Structural Database. [16] Kudielka, H. (1977), Z. Kristallogr., 145, 177. [17] Rappenglück, M.A. et al., 2013, Abstract #5055. 76th Annual Meteoritical Society Meeting. [18] Ivanova, M.A. et al. (2001), Abstract #1957. 32nd Lunar & Planetary Science Conference. [19] Chi Ma et al. (2011), American Mineralogist, 96, 709-715. [20] Sweeney Smith, S.A. et al. 2010. Abstract #1877 41st Lunar & Planetary Science Conference. [21] Kahlenberg, V. et al. 2000. American Mineralogist 85, 1061-1065. [22] Deloule, E. et al. (2001), Geochimica et Cosmochimica Acta, 65, 1833-1838. [23] Kamo, S.L. et al. (2011), Earth Planet. Sci. Letters, 310, 401-408. [24] Fehr, K.T. et al. (2004), Aufchluss, 55, 297-303.