

**Univerzita Karlova**  
**Přírodovědecká fakulta**

Studijní program: Geologie (P0532D330012)

Studijní obor: D-GEOL (0532VD330012)



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Chemické a fyzikální vlastnosti impaktových skel  
Chemical and Physical Properties of Impact Glasses

Disertační práce

Vedoucí práce: RNDr. Roman Skála, Ph.D.

Praha, 2021

**Charles University**

**Faculty of Science**

Study programme: Geology

Branch of study: D-GEOL



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Doctoral thesis

Supervisor: RNDr. Roman Skála, Ph.D.

Prague, 2021

## Statement of authorship

I, Šárka Křížová, declare that this thesis, presented for the Ph.D. degree at Charles University in Prague, is a result of my original research and was written by myself and that all the literary sources were cited properly. Neither this thesis nor its substantial part has been submitted to fulfill requirements for other academic degrees and has not been previously submitted to Charles University in Prague or any other institution.

## Prohlášení

Prohlašuji, že jsem závěrečnou práci s názvem „Chemické a fyzikální vlastnosti impaktových skel“ zpracovala samostatně, pod vedením svého školitele RNDr. Romana Skály, Ph.D. a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V ..... dne.....

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Ing. Šárka Křížová

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## Preface

This thesis is a collection of published articles focused on three types of impact glasses: tektite-like glasses from the Zhamanshin impact structure, moldavites, and Muong Nong-type Australasian tektites from Laos. The topics covered include the determination and discussion of their major-, minor- and trace-element compositions, presence and characterization of mineral inclusions, and the evaluation of the contents of suspect meteoritic components either in the glass structure or in the form of inclusions within the glasses. In addition to the impact glasses, also their potential target rocks have been characterized. The thesis summarizes seven years of my study at the Institute of Geochemistry, Mineralogy and Material Resources, Charles University in Prague. Most of the works were carried out at the Institute of Geology of the Czech Academy and the Czech Geological Survey. Since September 2014, I was engaged in research that has resulted in the publishing of the attached papers. I completed and submitted this dissertation in June 2021.

As a part of my training in the subject of impact crating and related shock metamorphic effects, I visited the Ries Crater Museum in Nördlingen and Center for Ries Crater and Impact Research Nördlingen (ZERIN), where core samples from drill holes in the impact crater are stored including the 1973 scientific drilling to a depth of 1,206 meters. Also, I visited the Savannakhet Dinosaur Museum in Laos with a collection of large Muong Nong-type tektites, the House of Gems in Bangkok (Thailand) hosting a collection of Australasian tektites including the two largest tektites ever found, and the Moldavite Museum in Český Krumlov. For the understanding of the excavation and modification stages of impact crater formation, I visited the Altenburg, Aumühle, Gundelsheim, Otting, and Polsingen quarries where I had the opportunity to observe various types of ejecta deposits (e.g., Bunte Breccia, suevite) as well as megabreccia blocks in the structural rim of the Ries complex crater. The visit also allowed me to examine the mechanisms under which individual types of polymict ejecta had been emplaced as well as the role of water in the crater formation process. In particular, I have investigated the surface striations formed along the contact between the Bunte Breccia and underlying flat-lying Malmian limestone, contacts of Bunte Breccia with suevite, and degassing pipes cross-cutting suevite deposited over Bunte Breccia.

A great experience was a field trip to sample Australasian tektites for the purpose of the Czech Science Foundation project No. 17-27099S in Thailand, Laos and Cambodia in February 2017. During this field trip, selected localities crucial for a comprehensive understanding of the geological situation of the occurrence of tektites have been visited. Simultaneously, the well-located tektite samples have been collected for later geochemical study. I was a member of a research group of the Institute of Geology of the Czech Academy of Sciences scientists participating in the Czech Science Foundation projects No. 13-22351S and No. 17-27099S. Principally, I was responsible for measurement of major element composition with an electron probe microanalyzer and documenting of the appearance and microstructure of the samples.

I presented my results at three international conferences (The 25<sup>th</sup> Goldschmidt Conference, Prague, 2015; The 79<sup>th</sup> Annual Meeting of the Meteoritical Society, Berlin, 2016; and the European Planetary Science Congress, Berlin, 2018).

I was awarded the Outstanding Student Poster Award at the European Planetary Science Congress (EPSC 2018) held in Berlin on September 16–21, 2018. The award honored my results in the study of Australasian tektites – Sulfide globules in Muong Nong-type tektites from Laos. One part of the study has already been published in the *American Mineralogist* journal and the second part focused on the HSE contents in globules is pending submission.

Next to the eight enclosed scientific papers that I (co)authored and which represent the principal part of the submitted thesis, the thesis also includes a brief *Introduction* to the problems of impact processes and impact glasses and their origin, where the relevant background information and terminology are provided. The main topics and scientific questions of this thesis are summarized in the *Aims of the research*. The *Methodology* part provides details of analytical methods, principles and different experimental procedures used in this study. The microstructure of the samples and the potential admixture of the meteoritic component into studied impact glasses are discussed in the *Results and discussions* section. Eventually, the most significant outcomes are highlighted in *Conclusions*. The main part of the thesis consists of eight articles in peer-reviewed journals organized to the *Appendix*. Chapters *Results and discussions* and *Conclusions* of this thesis provide scientific background information of the results presented in publications included in the *Appendix*.

## Publications included in this thesis

- I. **Jonášová Š.**, Ackerman L., Žák K., Skála R., Ďurišová J., Deutsch A. and Magna T. (2016) Geochemistry of impact glasses and target rocks from the Zhamanshin impact structure, Kazakhstan: Implications for mixing of target and impactor matter. *Geochimica et Cosmochimica Acta* **190**, 239–264. **impact factor after Journal Citation Reports (abbr. IF): 4.609; citations after the Web of Science (abbr. WoS): 14**
- II. Magna T., Žák K., Pack A., Moynier F., Mougél B., Peters S., Skála R., **Jonášová Š.**, Mizera J. and Řanda Z. (2017) Zhamanshin astrobleme provides evidence for carbonaceous chondrite and post-impact exchange between ejecta and Earth's atmosphere. *Nature Communication* **8**: 227, 1–8. **IF 12.353; WoS: 10**
- III. Žák K., Skála R., Řanda Z., Mizera J., Heissig K., Ackerman L., Ďurišová J., **Jonášová Š.**, Kameník J. and Magna T. (2016) Chemistry of Tertiary sediments in the surroundings of the Ries impact structure and moldavite formation revisited. *Geochimica et Cosmochimica Acta* **179**, 287–311. **IF 4.609; WoS: 28**
- IV. Ackerman L., Magna T., Žák K., Skála R., **Jonášová Š.**, Mizera J. and Řanda Z. (2017) The behavior of osmium and other siderophile elements during impacts: Insights from the Ries impact structure and central European tektites. *Geochimica et Cosmochimica Acta* **210**, 59–70. **IF 4.690; WoS: 9**
- V. Skála R., **Jonášová Š.**, Žák K., Ďurišová J., Brachaniec T. and Magna T. (2016) New constraints on the Polish moldavite finds: a separate sub-strewn field of the central European tektite field or re-deposited materials? *Journal of Geosciences* **61**, 171–191. **IF 0.609; WoS: 12**
- VI. **Křížová Š.**, Skála R., Halodová P., Žák K. and Ackerman L. (2019) Near end-member shenzhuangite, NiFeS<sub>2</sub>, found in Muong Nong-type tektites from Laos. *American Mineralogist* **104**, 1165–1172. **IF 2.631; WoS: 1**
- VII. Ackerman L., Skála R., **Křížová Š.**, Žák K. and Magna T. (2019) The quest for an extraterrestrial component in Muong Nong-type and splash-form Australasian tektites from Laos using highly siderophile elements and Re–Os isotope systematics. *Geochimica et Cosmochimica Acta* **252**, 179–189. **IF 4.258; WoS: 3**
- VIII. Žák K., Skála R., Pack A., Ackerman L. and **Křížová Š.** (2019) Triple oxygen isotope composition of Australasian tektites. *Meteoritics & Planetary Science* **54**, 1167–1181. **IF 2.318; WoS: 4**

Number of citations after the WOS as of May 21, 2021.

## Definition of terms for the purpose this thesis

**impactites** – impactite is a collective term for all materials affected or formed by a hypervelocity impact resulting from the collision of planetary bodies, e.g. shocked basement rocks, impact melt rocks, lithic impact breccias (Stöffler and Grieve, 2007; Osinski and Pierazzo, 2013)

**tektites** – tektites are a sub-class of impact melt glasses; they are small (millimeter to meter-sized) glassy bodies ejected to greater distances from the crater and spread over larger geographic areas – strewnfields (Bouška et al., 1987; French, 1998; Stöffler and Grieve, 2007)

**splash-form-type tektites** – a type of tektites, which are centimetre-sized objects shapes of spheres, droplets, teardrops, dumbbells (Lacroix, 1935; Stauffer and Butler, 2010)

**tektite-like glass** – glassy objects that possess tektite appearance yet they are deposited inside a crater or in its immediate vicinity

**Muong Nong-type tektites** – have an irregular, blocky shapes and a layered structure. The alternation of dark and light colored layers are visible in thin sections (e.g., (Lacroix, 1935; Barnes, 1961; Barnes and Pitakpaivan, 1962; Wasson, 1991; Koeberl, 1992)

**Suevite** – allochthonous polymict impact breccia consisting of impact melt particles set in lithic matrix (Osinski and Pierazzo, 2013)



## List of abbreviations

AAT – Australasian tektites

CET – Central European tektites

EPMA/WDS – electron probe microanalyzer equipped with wavelength-dispersive X-ray spectrometers

HSE – highly siderophile elements (Ru, Rh, Pd, Re, Os, Ir, Pt, and Au)

LA-ICP-MS – laser ablation inductively coupled plasma mass spectrometry

LILE – large-ion lithophile elements (K, Rb, Sr, Cs, Ba)

MNT – Muong Nong-type tektite

PGE – platinum group elements (Ru, Rh, Pd, Os, Ir, Pt)

RS – Raman spectrometry

SEM/BSE – scanning electron microscopy with a backscattered electron detector

SEM/CL – scanning electron microscopy with a cathodoluminescence detector

SEM/EBSD – scanning electron microscopy with an electron backscatter diffraction detector

SEM/EDS – scanning electron microscopy with X-ray microanalysis

SEM/SE – scanning electron microscopy with a secondary electron detector

SF – splash-forms

XRD – X-ray diffraction

ZIS – Zhamanshin impact structure



One of two largest Muong Nong-type tectites ever found now hosted at the House of Gems in Bangkok (Thailand)



Typical field appearance of the Muong Nong-type tectite as illustrated by the find at a sandpit close to Muang Phin

## Abstract

This work deals with microstructural features, chemistry and the search for traces of a meteoritic component in proximal tektite-like glasses from the Zhamanshin impact structure (Kazakhstan; further abbreviated as ZIS), and tektites from two strewn fields – moldavites (Czech Republic) and Australasian tektites (Laos; further abbreviated as AAT).

Detailed microstructural observations and subsequent chemical and mineralogical studies of various types of inclusions were also performed; these inclusions were mostly found in the studied types of glasses for the first time ever.

The aim of this PhD thesis was to (i) describe the microstructure of all studied glasses with a focus on yet unobserved microstructural phenomena, and (ii) try to determine the admixtures of meteoritic components in these glasses. In addition, the available target rocks, which could be a source of moldavites or AAT, were also studied. The microstructures of the studied glasses mutually differ. This is due to a diversity of parent materials and different glass formation conditions occurring during a particular impact event. A new type of "composite splash-form" has been identified among the ZIS glasses, whose chemical composition does not fit into the previously defined groups of irghizites or basic "splash-forms". For the first time ever, mineral bassanite (monoclinic  $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ ) was found in irghizites, which was identified on the basis of X-ray diffraction and Raman spectroscopy. Among notable contributions of this work is the discovery of two types of sulfide inclusions in MN AAT. Type 1 is composed of troilite (FeS), shenzhuangite ( $\text{NiFeS}_2$ ; a rare mineral that has only been identified in highly shocked Suizhou L6 chondrite) and a "monosulfide solid solution" (mss). Type 2 inclusions are composed of chalcopyrite ( $\text{CuFeS}_2$ ), as yet unspecified FeS phase and a monosulfide solid solution (mss). Type 1 inclusions appear to be of extraneous (meteoritic) origin whilst type 2 inclusions are presumably of terrestrial origin. This thesis also describes inclusions of unusual shapes, structures and compositions found in MN AAT from Laos.

One of the aims of the work was to compare a complex geochemical relationship of moldavite tektites and a set of Miocene sedimentary rocks from the area of the Ries crater representing possible CET source materials. The results support sediments as precursor materials of moldavites, but at the same time they require a process that would be able to

explain the enrichments in volatile elements in moldavites compared with the chemistry of the expected sediments.

Furthermore, the newly found Polish moldavite, which extends the largest distance with known occurrences of moldavites from ~ 420 km to ~ 475 km from the center of the Ries crater, was also characterized in greater chemical and structural details. The chemical composition of this find is indistinguishable from the general compositional trends of moldavites from other strewn sub-fields. However, there are inhomogeneous areas with increased contents of calcium and magnesium, which have so far been observed only in South Bohemian moldavites.

The presence or absence of the meteoritic component was tested by studying PGE, HSE, the isotopic system Re–Os, oxygen isotope compositions and chromium isotope systematics in glasses for selected specimens. Unambiguous identification of extraterrestrial material in tektites and tektite-like glasses is possible if sufficiently high contents of PGE and HSE are present, which allow a meaningful calculation of diagnostic parameters. The use of combined HSE abundances and Os isotope systematics can be affected by elemental fractionation or even significant loss of HSE from tektite glass in early stages of glass formation. The results obtained for moldavites and Australasian tektites indicate a possible minor addition of a meteoritic component from the projectile, although the nature of the projectile cannot be unequivocally characterized and/or quantified. Traces of the extraterrestrial component and the type of projectile were determined only for irghizites (proximal glasses from the ZIS) that were identified to be contaminated by a projectile of carbonaceous chondrite character, specifically CI type as devised by chromium isotope data.

## Abstrakt

Tato práce se zabývá studiem mikrostrukturních rysů, chemismem a hledáním stop meteoritické komponenty v impaktových sklech pocházejících z kráteru Žamanšin (Kazachstán), vltavínech (Česká republika) a australsko-asijských tektitech (Laos). Byla provedena detailní mikrostrukturní pozorování a následné chemické a mineralogické studie různých typů inkluzí, které byly ve studovaných typech skel nalezeny většinou poprvé.

Cílem této Ph.D. práce bylo nejen popsat mikrostrukturu všech studovaných skel a soustředit se na doposud nepozorované a v dostupné existující literatuře nepopsané mikrostrukturní jevy, ale zároveň se v těchto skel pokusit zjistit příměsi meteoritické komponenty. Kromě toho byl také studován dostupný zdrojový materiál, který by mohl být zdrojem vltavínů a AAT.

Mikrostruktura všech studovaných skel se navzájem liší. To je způsobeno různými zdrojovými materiály a odlišnými podmínkami vzniku skel. U skel ze ZIS byl identifikován nový typ „composite splash-forms“, který svým chemickým složením nezapadá do skupiny irgizitů ani bazických „splash-forms“. Nově byl v irghizitech nalazen vměstek, který byl na základě rentgenové difrakce a Ramanovy spektroskopie identifikován jako bassanit (monoklinický  $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ ). Jeden z nejdůležitějších výsledků této práce představuje objevení dvou typů sulfidických inkluzí v MN AAT. Typ 1 je složen z troilitu ( $\text{FeS}$ ), shenzhuangitu ( $\text{NiFeS}_2$ ; vzácný minerál, který byl identifikován pouze v chondritu Suizhou L6) a „monosulfide solid solution“ (mss). Druhý typ inkluzí je složen z chalkopyritu ( $\text{CuFeS}_2$ ), dále z dosud blíže nespécifikované  $\text{FeS}$  fáze a „monosulfide solid solution“ (mss). Se značnou dávkou pravděpodobnosti je možné se domnívat, že inkluze typu 1 jsou meteoritického původu, kdežto inkluze typu 2 jsou původu pozemského. V disertační práci jsou také studovány inkluze neobvyklých tvarů, struktury a složení nalezené v MN AAT z Laosu.

Jedním z cílů práce bylo komplexní porovnání chemických dat vltavínů a sady miocénních sedimentárních materiálů z oblasti kráteru Ries, představujících možné zdrojové horniny. Výsledky identifikují sedimentární materiály jako hlavní zdrojový materiál vltavínů, současně však vyžadují naložený další proces, který je nezbytný k vysvětlení obohacení těkavými složkami ve vltavínech v porovnání s chemismem zdrojových sedimentů. Dále byl blíže charakterizován nově nalezený polský vltavín, který

prodlužuje největší vzdálenost známých výskytů vltavínů z ~420 km na ~475 km od centra kráteru Ries. Chemické složení tohoto nálezu je nerozeznatelné od obecných kompozičních trendů vltavínů z jiných dílčích pádových polí. Nachází se v něm ovšem nehomogenní oblasti se zvýšenými obsahy vápníku a hořčíku, které byly dosud pozorovány pouze u jihočeských vltavínů.

Přítomnost či absence meteoritické komponenty byly určeny pomocí studia PGE, HSE, izotopického systému Re–Os, isotopového složení kyslíku a ve vybraných případech i izotopové systematiky chrómu. Jednoznačná identifikace přítomnosti mimozemského materiálu v tektitech a ve sklech podobných tektitům je možná, pokud jsou přítomny dostatečně vysoké obsahy PGE a HSE, které umožňují smysluplný výpočet diagnostických parametrů. Použití HSE i izotopové systematiky Os může být velmi ovlivněno prvkovou frakcionací nebo dokonce významnou ztrátou HSE z tektitového skla v jeho rané fázi tvorby. Zjištěné výsledky u vltavínů a australsko-asijských tektitů svědčí o možném přídavku meteoritické komponenty projektilu, i když ji nelze podrobněji charakterizovat ani kvantifikovat. Stopy extra-terestrické složky a typ projektilu byl určen pouze u irghizitů – proximálních skel pocházejících z kráteru Žamanšin, kde s jistotou lze konstatovat, že projektilem byl uhlíkatý chondrit a na základě izotopové systematiky chrómu je navrhován chondrit blízký typu CI.

## Conferences attended

As the main author, I presented my results at three international conferences: Goldschmidt, Prague, 2015; The Meteoritical Society, Berlin, 2016; European Planetary Science Congress, Berlin, 2018.

### **Goldschmidt, 2015**

*Author of poster:* Š. **Jonášová**, L. Ackerman, K. Žák, R. Skála, J. Ďurišová, A. Pack and T. Magna (2015), Highly siderophile elements and triple-oxygen isotopes of tektite-like glasses from the Zhamanshin impact structure, Kazakhstan, Goldschmidt, Prague, August 16 – 21, 2015.

*Co-author of poster:* R. Skála, K. Žák, Š. **Jonášová**, J. Ďurišová, L. Ackerman, Z. Řanda, J. Mizera, J. Kameník, T. Magna (2015), Differences in chemistry of the Ries area sediments and central European tektites revisited, Goldschmidt, Prague, August 16 – 21, 2015.

### **77<sup>th</sup> Annual Meeting of the Meteoritical Society, 2015**

*Co-author of presentation:* T. Magna, K. Žák, A. Pack, L. Ackerman, R. Skála, Š. **Jonášová**, J. Ďurišová, Z. Řanda, J. Mizera (2015), Triple-oxygen and highly siderophile elements in Moldavites and irghizites: Clues for source materials of tektites and other impact-related glasses, 77<sup>th</sup> Annual Meeting of the Meteoritical Society Casablanca, Morocco, September 8 – 13, 2014.

### **46<sup>th</sup> Lunar and Planetary Science Conference, 2015**

*Co-author of poster:* L. Ackerman, K. Žák, Š. **Jonášová**, J. Ďurišová, R. Skála and T. Magna (2015), Highly siderophile element geochemistry of impact-related glasses and target rocks from Zhamanshin impact structure, Kazakhstan. 46<sup>th</sup> Lunar and Planetary Science Conference (2015), Houston, March 16 – 20, 2015

**The Meteoritical Society, 2016**

*Author of poster:* Š. **Jonášová**, L. Ackerman, K. Žák, R. Skála, T. Magna, A. Pack & A. Deutsch: Constraints on the Nature of the Projectile Using Siderophile Elements and Triple-oxygen Isotopes: Zhamanshin impact structure, Kazakhstan. The Meteoritical Society. 79<sup>th</sup> Annual Meeting; Berlin, August 8 – 12, 2016.

*Co-author of poster:* R. Skála, Š. **Jonášová**, K. Žák, J. Ďurišová, T. Brachaniec & T. Magna: A New Moldavite Sub-Strewn Field in Lower Silesia, Poland. The Meteoritical Society. 79<sup>th</sup> Annual Meeting; Berlin, August 8 – 12, 2016.

**European Planetary Science Congress, 2018**

*Author of poster:* **Křížová Š.**, Skála R., Ackerman L., Žák K. and Magna T., Sulfide globules in Muong Nong-type tektites from Laos. European Planetary Science Congress. Berlin 2018. Abstract no.: 327.

*Co-author of poster:* Skála R., **Křížová Š.**, Matoušková Š., Trnka M., Žák K., Variability within and between large bodies of Muong Nong-type tektites in Laos. European Planetary Science Congress. Berlin 2018. Abstract no.: 835.



## Acknowledgments

I could not have achieved my current level of success without a strong support group of important people. I would like to thank my supervisor RNDr. Roman Skála, Ph.D. for his support, helpful advice during all phases of this research, never-ending discussions and for critical comments, which produced major improvements. I am very grateful to doc. Mgr. Lukáš Ackerman, Ph.D. for his excellent guidance during isotopic analysis. I also wish to thank RNDr. Karel Žák, CSc., who reviewed the various versions of the evolving manuscripts. Dr.sc.nat. Tomáš Magna aided in the critical reading of the manuscript and provided some valuable suggestions. I would like to thank you all for your wonderful cooperation as well.

I would like to thank RNDr. Milan Trnka for guidance, assistance and invaluable advice in the field during the expedition to Thailand, Laos and Cambodia. I also thank him for providing samples of sediments, moldavites, and glasses from the Zhamanshin impact crater that were extremely beneficial throughout this study.

I would also like to thank John Hora, Ph.D. for linguistic and stylistic adjustments of the early version of the thesis and Dr.sc.nat. Tomáš Magna for language reviewing its final version.

Finally, I would like to thank my parents, my family and friends for being helpful and supportive during my study. Thank you all for your unwavering support.

This research was funded by the Czech Science Foundation Projects No. 13-22351S to Tomáš Magna and No. 17-27099S to Roman Skála and co-financed by institutional support RVO 67985831 of the Institute of Geology of the Czech Academy of Sciences.



## 1 Introduction

At present, there are worldwide about 190 confirmed terrestrial impact structures (Earth Impact Database, 2021). This clearly manifests that impact processes have an enormous influence on the geological and biological history of the Earth and are a significant geological phenomenon that gained widespread recognition in the early 20<sup>th</sup> century. Only in the 1970s and 1980s several specific shock metamorphic criteria and some dozens of unequivocally confirmed terrestrial impact sites were recognized (e.g., French and Short, 1968; Dence et al., 1977; Osinski and Pierazzo, 2013). Nevertheless, the competing crypto-volcanic hypothesis of impacts survived to some degree until the end of the 20<sup>th</sup> century. Countless extraterrestrial objects (comets, asteroids, meteorites, interplanetary dust, and maybe suspect intergalactic bodies) fell on the Earth's surface, shaped the geological landscape, affected the evolution of life throughout geological history and formed impact craters. On the other hand, terrestrial geological processes (erosion, tectonics, volcanism) act to obliterate most of these impact craters. Also, if one considers the Earth area covered by deep waters, a significant amount of extraterrestrial matter which would otherwise produce impact structures went lost after falling to sea without producing craters (Melosh, 1989).

A hypervelocity impact crater on the Earth is a structure formed by an extraterrestrial projectile that is large enough (typically >50 m for a stony object and >20 m for an iron body) and passes through the Earth's atmosphere with no or little deceleration and strikes at the original velocity (>11 km s<sup>-1</sup>) (French, 1998; Stöffler et al., 2002; Osinski and Pierazzo, 2013). The crater is produced by intense shock waves where transient pressures may exceed 500 GPa at the impact point and maybe as high as 10–50 GPa throughout the surrounding target rock. The transition of a shock wave affects terrestrial rocks, which consequently undergo elastic or plastic deformation depending on the shock wave-induced strain applied (French, 1998; Kenkmann et al., 2018).

Unique and permanent petrological and geochemical deformations/criteria arise in the target rocks. The terrestrial rocks expand and interact with the original ground surface to set a large volume of the target rock into motion, thus excavating the impact crater (French, 1998). Typically, the formation of an impact crater may be divided into three main stages overlapping in time and space: (1) contact and compression; (2) excavation; and (3)

modification (Melosh, 1989; French, 1998). (1) The contact and compression stage begins at the moment when the moving projectile hits the ground surface. A high-speed impact causes a sudden compression of the projectile and the target materials at the impact surface. It generates a shock wave that propagates upwards through the projectile and downwards to the target material/rocks. Resulting thermodynamic changes are irreversible and almost instantaneous. The target material changes from the initial state to the shocked state. (2) Excavation stage is a part of the process during which the actual impact crater is formed/opened up by complex interactions between the expanding shock waves and the original ground surface. The shock waves expand rapidly through the target rock and tend to deflect the particle trajectories towards the surface; at the same time, they push the material into the target and expel material from the expanding crater. (3) Modification is the final stage of the cratering process. In this stage, the crater collapses due to gravity-driven modification of the unstable cavity formed during excavation (French, 1998; Osinski and Pierazzo, 2013; Kenkmann and Wulf, 2018). Two principal types of crater can be recognized based on morphology and size, simple or complex (e.g., Melosh, 1989; Grieve and Pesonen, 1992).

Tektites generally arise at early-stage shock compression of target rocks. They are ballistically ejected due to acceleration after decompression. The heat during shock decompression is responsible for impact melting and vaporization phenomena. High-velocity turbulent flow results in impact melt bodies of a generally mixed composition, corresponding to the volume of the target that was melted (e.g., Stöffler, 1984).

However, not every impact is accompanied by the formation of glasses or tektites. Indeed, only a small number of the impact events produced distal and/or proximal impact glasses. Impact glasses which are, in general, important and valuable in the field of cosmic and planetary research, can be divided into proximal glasses, which were found close to the impact structure (proximal glassy impactites) and glasses of distal origin (distal glassy impactites). The boundary between these two principal groups is arbitrarily set to 5 radii of the impact crater (Melosh, 1989; Montanari and Koeberl, 2000). These impactites differ from each other morphologically, chemically and structurally. Representatives of proximal glassy impactites in this thesis are glass shards in suevites from the Ries crater and glasses from the Zhamanshin impact structure.

One of typical examples of distal ejecta are splash-form tektites (Dressler and Reimold, 2001). Tektites were named by Suess (1900) from the Greek word for “melted” (Bouška, 1972). They represent natural silicate glasses formed by the melting of topmost sedimentary rocks at the target area during the hypervelocity impact of a cosmic body. This is, at present, the most widely accepted theory of tektite origin being first published by Spencer (1933). The process itself is very fast and complex. Currently, it is generally assumed that tektites are formed by the action of heavily compressed and heated air, pushed in front of the impacting meteorite (bow shock), on the uppermost horizon of the sedimentary pile at the point of the impact (David, 1973; Delano and Lindsley, 1982; David, 1988). From a chemical point of view, the compositions of tektites largely reflect those of target materials (e.g., Engelhardt et al., 1987; Engelhardt et al., 2005; Koeberl, 2014), sometimes with depletion/enrichment of individual elements relative to the source rocks depending on their respective evaporation and condensation temperatures (Žák et al., 2016). Tektites may also display contamination derived from a projectile though the proportion of the extraterrestrial component does not exceed ca 1 percent (e.g., Koeberl, 1993; Koeberl and Shirey, 1993; Foriel et al., 2013; Ackerman et al., 2017).

Tektites are traditionally classified into four major morphological groups (e.g., Glass, 1984; Koeberl, 2014):

(1) normal or splash-form, whose shapes (e.g., spherical, teardrop, dumbbell, disc) result from solidification of rotating melt particles; they have more homogeneous internal structures than other types;

(2) ablated-form (or aerodynamically-shaped) tektites representing melts of the tektite glass shaped by atmospheric re-entry. These tektites are only found in the Australasian strewn field (e.g., Chapman and Larson, 1963; Glass, 1990)

(3) Muong Nong-type (or layered) tektites are usually considered to be markedly larger than normal tektites and are of chunky or blocky appearance with heterogeneous textures and chemical compositions; yet most of found samples represent only small fragments of possibly disintegrated large blocks (e.g., Futrell, 1986; Koeberl, 1986; Wasson, 1991)

(4) Microtektites are defined as tektites smaller than 1 mm in diameter and are critical for defining the extent of the strewn fields (e.g., Glass, 1967; Glass et al., 1979; Glass and Zwart, 1979). In addition, their spatial distribution provides a clue in the

estimation of the possible source craters location (e.g., Glass and Pizzuto, 1994). Microtektites have been preserved only in deep-sea sediments and the range of their bulk chemical compositions is much wider than tektites from the same strewn field found on land (see, e.g., O'Keefe, 1969; Frey et al., 1970; Glass and Zwart, 1979; Glass et al., 2004; Folco et al., 2009; Moynier et al., 2010)

Tektites occur in well-defined, geographically limited areas, so-called strewn fields (Glass et al., 1979; Glass et al., 1991). There are four major tektite strewn-fields: the North American strewn field (~35 Myr old), the Central European strewn field (~14.8 Myr old), the Ivory Coast strewn fields (~1.07 Myr old) and the Australasian strewn field (~0.78 Myr old) (Glass, 1984). However, only three source craters are known, the Chesapeake Bay crater (USA) that is associated with georgiites and bediasites, the Ries Crater (Germany), which is linked to moldavites, and the Bosumtwi crater (Ghana) related to ivorites. Surprisingly, no confirmed impact structure is unequivocally associated with Australasian tektites (Chapman and Larson, 1963; Bouška et al., 1968; Koeberl, 1986; Glass et al., 1995; Albin et al., 2000; Montanari and Koeberl, 2000) and several recent studies provided opposed views on its possible location (e.g., Mizera et al., 2016; Ackerman et al., 2019; Sieh et al., 2020).

Impact bodies, which formed impact structures, or at least their major portions mostly melted and/or evaporated during the impact on the Earth's surface (Melosh, 1989; French, 1998; Osinski and Pierazzo, 2013). The remaining solid fragments of the extraterrestrial material either could mix with target rocks or get trapped in the structure of the formed glasses (i.e., impact melt pockets, dikes or sheets) or in rocks underneath the crater bottom (Schmidt et al., 1997; McDonald et al., 2007).

This thesis primarily focuses on the study of the inner structure and chemical composition of proximal tektite-like glasses from the Zhamanshin impact structure (ZIS) and tektites from two strewn fields – the Central European strewn field (moldavite tektites, MT) and the Australasian strewn field (Australasian tektites, AAT). It aims to track contamination by an impactor and interactions with the atmosphere and target rocks in these glasses.

## 1.1 Proximal tektite-like glasses from the Zhamanshin impact structure

The ZIS impact structure with an estimated age of ~1 Ma (Storzer and Wagner, 1977; Koeberl and Storzer, 1987; Deino et al., 1990) is situated approximately 200 km north of the Aral Sea and about 40 km southwest of the town of Irghiz. This semi-arid region has a wide diversity of heterogeneous target rocks involved in the impact event. Quaternary loess and lake sediments fill the crater, while the rim consists of allogenic breccia with Paleozoic rock fragments and faulted/fractured Paleozoic sediments together with impact glasses. The basement consists of Lower Neoproterozoic to Lower Paleozoic volcano-sedimentary series and the overlying ca 100–150 m thick platform of Upper Paleozoic volcano-sedimentary series, Cretaceous sandstones, and marls, covered by Paleogene sands, clays, and locally sandstones (e.g., Florenski, 1977; Florenskii and Dabizha, 1980). The impact structure is a circular depression and consists of two funnel-like features, the inner has a diameter of 5.5–6.0 km, and the outer has a diameter of 13–14 km (Florenskii and Dabizha, 1980; Masaitis et al., 1984; Garvin and Schnetzler, 1994). The impact structure itself today forms a shallow roughly circular depression in terms of terrain morphology and reflects late landslide processes (e.g., erosion, post-impact gravity movements of poorly consolidated sediments).

This impact event did not create a strewn field of tektites *sensu stricto*, but various types of impact glasses, often also called tektite-like glasses, were found in the vicinity and within the crater.

Principally, three major groups of tektite-like glasses are distinguished in this crater: (1) irghizities that formed by coalescence of < 1mm sized glass droplets reaching ~ 69–76 wt.% SiO<sub>2</sub>; (2) basic splash-forms that display no evidence of coalescence of the droplets, yet their inner structure is fluidal; this type of glasses has a rough surface affected by glass corrosion and ~ 53–58 wt.% SiO<sub>2</sub>; (3) zhamanshinites, which are blocky pieces up to 50 cm large with variable composition with ~ 40–80 wt.% SiO<sub>2</sub>, and partly porous structure; they have been divided into Si-rich and Si-poor varieties. The so-called blue zhamanshinites are a subgroup of Si-rich zhamanshinites (e.g., Koeberl and Storzer, 1987; Koeberl, 1988; Zolensky and Koeberl, 1991; Vetvicka et al., 2008).

## 1.2 Moldavite tektites, Central European strewn field

Moldavites were formed from the uppermost sedimentary rock layer during the Ries impact event in the Middle Miocene ( $14.808 \pm 0.038$  Ma; (Rocholl et al., 2018; Schmieder et al., 2018)). The Ries impact structure in Bavaria (Germany) is ~26 km wide (Stöffler et al., 2013). Moldavites occur in several so-called sub-strewn fields, which are located in e.g. South Bohemia, Western Moravia, the Cheb Basin, the Horn area in Upper Austria, Lusatia in Germany, and several scattered finds were also reported at various places in Bohemia and Poland (e.g., Bouška and Konta, 1986; Koeberl et al., 1988; Trnka and Houzar, 1991; Störr and Lange, 1992; Lange, 1995; Trnka and Houzar, 2002; Řanda et al., 2008; Skála et al., 2009; Brachaniec et al., 2014, 2015; Skála et al., 2016). Among those scattered finds on the territory of the Czech Republic, the moldavites from Kobylišy (Žebera, 1972) and Jeviněves sandpits (Žák et al., 1999) as well as those from a river terrace of the Berounka river near Skryje (Ložek and Žák, 2011) should be mentioned. The chemical diversity of moldavites from sub-strewn fields is a consequence of the chemical variability of source sediments of the Upper Freshwater Molasse at the site of impact (Žák et al., 2016). However, the differences in the chemical composition between moldavites from individual sub-strewn fields probably also reflect such phenomena like slightly different selective volatilization due to assumed variable thermal histories (Philpotts and Pinson, 1966). Since the differences among moldavites from individual sub-strewn fields (corrosion, size, shape, color) are rather marginal, their common origin is assumed (Bouška et al., 1968).

## 1.3 Australasian tektites, Australasian strewn field

The Australasian tektite (hereafter abbreviated AAT) strewnfield is the youngest example of a tektite-forming event ( $0.78 \text{ Ma} \pm 0.028 \text{ Ma}$ , (Jourdan et al., 2019)) and covers by far the largest area where tektite of the same origin occur, estimated variously to cover at least 10% of Earth's surface (Folco et al. 2016; Goderis et al., 2017). Despite their young age, the intrinsic impact site of the projectile remains debated. There are a number of hypotheses about the location of this crater placing it usually to various locations in Laos, Vietnam, or China (e.g., Glass and Pizzuto, 1994; Lee and Wei, 2000; Ma et al., 2004; Son and Koeberl, 2005; Folco, Glass, et al., 2010; Mizera et al., 2016; Rochette et al., 2018; Ackerman et al., 2019; Sieh et al., 2020). The area where tektites and microtektites occur



extends from Indochina to Antarctica in a north-south direction and from Madagascar to Micronesia in an east-west direction, see Fig. 1 (e.g., Glass, 1984; Folco et al., 2016).

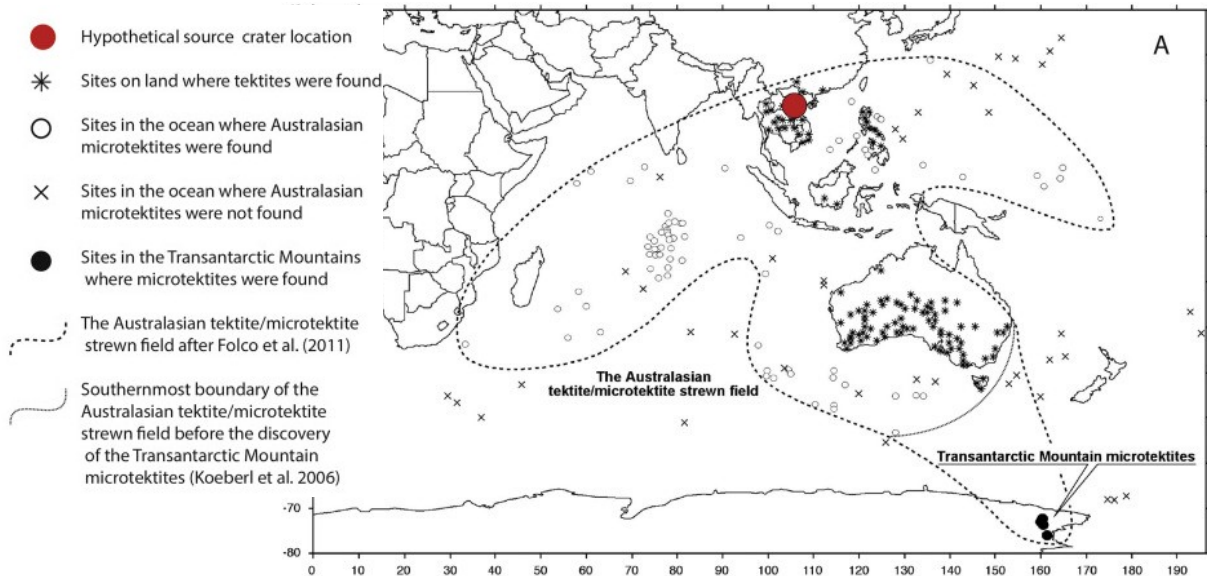


Figure 1: Australasian tectite and microtektite strewn field (Folco et al., 2016)

Three major morphological types recognized among cm-sized or larger AAT are— Muong Nong-type tektites, splash-forms, and ablated forms. Small splash-forms sized below 1 mm are called microtektites where occur in deep-sea sediments.

Muong Nong-type (MNT) Australasian tektites have a black color, an irregular, blocky appearance, and they are usually considerably larger than normal tektites. A typical feature of MNT tektites is their layered structure. In thin sections, dark- and light-colored layers alternate. The lighter areas contain more bubbles than the darker zones. Further evidence of incomplete homogenization is the occurrence of frothy lechatelierite (Koeberl, 1992). In some samples, the layers are stretched in the shape of folds or have a breccia-shaped structure (Futrell and Fredriksson, 1983). This type of tektites probably represents sprayed glass that did not fly far from the source crater.

Australasian splash-forms (SF) were shaped by rotation of the viscous melt and most of them have internal stresses. Splash-forms differ from MNT tektites not only in appearance, structural homogeneity, refractive index but also in chemical composition. Besides, MNT tektites are enriched in volatile compounds compared to splash-form tektites. These differences between both types reflect different formation conditions and possibly also different parent materials (e.g., Futrell, 1986; Koeberl, 1992).

It should be noted that area where MNT occur exclusively is rather small and mostly SF and MNT spatially coexist in wide regions (cf. Fig 1 in Schnetzler, (1992) or Fig. 2 in Fiske et al., (1999)).

#### **1.4 Study of microstructural features of glasses – inclusions and heterogeneities**

The locations of certain impact craters are as yet unknown and as a consequence, impact glasses and impactites in general are thus the only evidence of these impact events (e.g., the Alamo Breccia; Warme and Kuehner, 1998). The microstructure study of such impactites can help clarify the process of their formation and provide ultimate support for presence of the vanished or buried impact structure. Detailed examination of a thin section of impact glass sample using a polarizing microscope or SEM/BSE/EDS/EBSD may reveal inclusions or other structural features (e.g. internal structures, variable color and/or chemistry of glass, frequency, shape and distribution of bubbles or shock-metamorphic effects in mineral inclusions). Some tektites can contain relict grains of original target materials or minerals displaying shock metamorphic effects or can be contaminated by minor quantities of extraterrestrial materials. However, as mentioned above, the ages of the studied tektite groups differ (moldavites ~14.808 Ma; glasses from the ZIS ~ 1.0 Ma; AAT ~0.78 Ma) requiring evaluation whether these structural features are of primary or secondary origin (i.e. whether there is a corrosion of the glass or other weathering process). Primary inclusions encapsulated within tektites provide a rare opportunity to confirm the formation process of tektites (Chao et al., 1964; Ganapathy and Larimer, 1984). They simultaneously provide evidence of the degree of shock transformation and record important information such as temperature and pressure history during the formation of tektites (Cavosie, Timms, Ferrière, et al., 2018). Inclusions also can provide information about the source rocks and projectile type.

Inclusions in tektites and tektite-like glasses may be both oxygen-bearing (oxides and silicates) or oxygen-free (sulfides, phosphides, native metals). The occurrence of mineral inclusions points to an origin from sedimentary target rocks. Among most common inclusions in tektites, sorted alphabetically, are: baddeleyite (monoclinic  $ZrO_2$ ), coesite, cristobalite, (shocked) quartz, reidite, rutile, stishovite, wollastonite and zircon (e.g., Walter, 1965; Glass, 1972; Glass and Barlow, 1979; Halvorson and McHone, 1993; Swaenen et al.,

2010; Folco, Perchiazzi, et al., 2010; Gomez-Nubla et al., 2017; Cavosie, Timms, Erickson, et al., 2018; Cavosie, Timms, Ferrière, et al., 2018; Folco et al., 2018). During the cooling of the glass, partial oxidation or crystallization may have occurred. The inclusions are cracked or showed a partial disruption of the crystal structure (Bouška et al., 1987). Coesite and stishovite indicate high pressure during the formation of impactites, whereas cristobalite and tridymite are evidence of high temperature during the impact process (Glass and Wu, 1993; Swaenen et al., 2010; Folco et al., 2018).

So-called “metallic” spherules composed predominantly of kamacite (FeNi), schreibersite ((FeNi)<sub>3</sub>P) and troilite (FeS) were found in AAT splash-form philippinites from the Ortigas site near Manila and in indochinites from Dalat, South Vietnam. Based on Ni contents (10.1 and 12.9 %) in the kamacite phase, Chao et al., 1964 concluded that the Ni–Fe spherules were produced during meteorite impact and their origin is extraterrestrial (Chao et al., 1964). However, further study (Ganapathy and Larimer, 1983; Ganapathy and Larimer, 1984) determined trace element pattern as distinctly terrestrial implying that the spherules are not of the meteoritic origin. The Ni–Fe spherules were also found in the Aouelloul impact glass located in Mauritania, northwest Africa (Chao et al., 1966), in tektites from Isabela, Philippine Islands (Chao et al., 1962), and also in impact glasses from the Meteor Crater area, Arizona (Brett, 1967).

Mineral inclusions were found also in glass from ZIS. Oxygen-bearing inclusions are represented by quartz, (Fe,Cr,Ti)- and Fe-oxide particles and lechatelierite inclusions with and/or without bubbles. Sulfidic inclusions are rich in Ni and Fe and their size varies between few hundred nanometers to few micrometers in size (Jonášová et al., 2016). Gornostaeva et al. (2016) found inclusions of nickel phosphide in the condensate film coating of irghizites.

In MNT AATs, the inclusions are most abundant. The following minerals were identified in this particular type of tektites: quartz, corundum, rutile, zircon, monazite, chromite, coesite, cristobalite and tridymite (Walter, 1965; Glass, 1970; Glass, 1972; Glass and Barlow, 1979; Dass and Glass, 1999; Glass, 2000).

The only inclusions found in moldavites include quartz, lechatelierite particles and baddeleyite (Knobloch et al., 1988; Švardalová, 2007). Metallic or sulfidic inclusions have not yet been discovered in moldavites.

## 1.5 Meteoritic components

The presence of solid meteorite fragments in impactites directly in a crater is rare because the shock wave also passes through the meteoritic impactor and within fractions of a second most or all of the projectile melts or vaporizes due to post-shock heating; the amount of vaporized material depends on diameter, physical and chemical properties, and velocity of the projectile and impact angle (Montanari and Koeberl, 2000). If solid meteorite fragments are missing in impactites, some traces of extraterrestrial components may still be present being mixed into the target materials forming impact melt rocks or tektites in form of the chemical fingerprint (Montanari and Koeberl, 2000; Goderis et al., 2017). An admixture of minor or trace amounts of the meteoritic component in tektites is a consequence of the contact between the impactor and target during the earliest phase of formation of tektites. A small amount of the finely dispersed meteoritic melt or vapor is mixed with a much larger quantity of target rock. Geochemical methods that determine certain elemental and isotopic ratios in impact glasses are often used to identify the impactor in glasses. Unfortunately, the amount of data on the contents of the meteoritic component in tektites is limited (Tagle and Berlin, 2008; Koeberl, 2014). Owing to the extremely small amount of meteoritic matter trapped and dissolved into the tektite glass (commonly  $\ll 1\%$  by weight although contribution by as much as 0.6% was also advocated for the Ivory Coast tektites; Koeberl and Shirey, 1993), detection of a meteoritic component is extremely difficult (Montanari and Koeberl, 2000). In order to distinguish meteoritic vs. terrestrial features in glasses of impact origin including tektites, (1) the concentrations of selected diagnostic elements or ratios of isotopes in selected systems must be different enough in a meteorite relative to those in parental terrestrial target rock (Koeberl and Shirey, 1993; Moynier et al., 2009; Koeberl et al., 2012) and (2) these elements or isotopic ratios must be accurately and precisely analyzed, even at those low concentration levels that are observed in impact glasses. Therefore, identification of a meteoritic component in tektites is not trivial and it should be pointed out that conflicting identifications have been made for a number of impact structures and many identifications of a projectile type are highly ambiguous (Koeberl, 1998; Montanari and Koeberl, 2000).

Geochemical methods are often used to identify the impactor in glass, determined by certain isotopic and elemental ratios in impact glass. The admixture of extraterrestrial material in tektites can be proven by

(1) The presence of the elevated contents of (highly) siderophile elements (Ni, Co and Cr and HSE: Ru, Rh, Pd, Re, Os, Ir, Pt, and Au) in tektites in comparison with those in the target rocks. (e.g., Chapman and Scheiber, 1969; Koeberl and Shirey, 1993; Montanari and Koeberl, 2000; Amare and Koeberl, 2006; Ackerman et al., 2017; Ackerman et al., 2019). If the admixture of even minor quantities of extraterrestrial material into target rocks with upper continental crust HSE contents occurred during the impact process, the resulting impact melt rocks or breccias would show significantly elevated abundances of the HSEs and particularly PGEs. Interelement PGE ratios are then important discriminators in the detection and identification of a projectile (e.g., Palme et al., 1981; Lee et al., 2006). However, once abundances of siderophile elements in the target rocks are high or conversely impactites host only negligible siderophile element concentrations (e.g., typically certain types of achondrites), the unequivocal determination of projectile may pose a problem (Montanari and Koeberl, 2000).

(2) The Re–Os isotopic systematics have significantly improved the ability to detect and identify certain types of extraterrestrial materials in tektites and more generally impact glasses (Koeberl and Shirey, 1997; Shirey and Walker, 1998; Tagle and Hecht, 2006). The detection of the extraterrestrial material is based on the ratio of the radiogenic osmium isotope ( $^{187}\text{Os}$ ), compared to a nonradiogenic osmium isotope ( $^{188}\text{Os}$ ) (Koeberl, 2014). Meteorites have relatively lower Re and much higher Os abundances than terrestrial crustal rocks; Re/Os ratios of meteorites are less than or equal to 0.1, while the Re/Os ratio of terrestrial crustal rocks usually exceeds 10. Consequently,  $^{188}\text{Os}/^{187}\text{Os}$  isotopic ratios for certain types of meteorites (chondritic or iron meteorite) and terrestrial crustal rocks differ greatly. Achondrites, however, contain only low concentrations of PGE making the use of Os isotopes inappropriate (Montanari and Koeberl, 2000; Tagle and Hecht, 2006; Foriel et al., 2013; Koeberl, 2014).

(3) Unlike Re–Os isotope systematics, Cr isotopes are suitable not only for distinguishing between the presence or absence of an extraterrestrial component but also the ultimate determination of the projectile type. In contrast to the Earth's upper continental crust (UCC), meteorites contain large concentrations of Cr (up to ~1 wt.%). Chromium isotope abundances ( $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$ , and  $^{54}\text{Cr}$ ) are diagnostic for different meteorite groups (especially obvious in ordinary chondrites (types H and L), enstatite chondrites, and differentiated achondrites, and carbonaceous chondrites (see Shukolyukov and Lugmair,

1998; Montanari and Koeberl, 2000; Tagle and Hecht, 2006; Trinquier et al., 2008; Qin et al., 2010; Foriel et al., 2013; Koeberl, 2014; Magna et al., 2017; Mougél et al., 2018).

(4) Oxygen isotope ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ) ratios serve as a sensitive natural tracer to classify asteroidal and planetary materials in the Solar System but could also be used to help identify the impactor. While terrestrial or other planetary materials (e.g., terrestrial planets, differentiated asteroids or Moon) have  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  ratios displaying mass-dependent fractionation, undifferentiated materials (mostly chondrites) witnessed large mass-independent fractionation. These differences in O isotopic composition in the two principal reservoirs may result in negative  $\Delta^{17}\text{O}$  offsets in impact glasses. Such offsets could ultimately indicate the presence of impactor material with low  $\Delta^{17}\text{O}$  values or exchange with ambient air (Taylor and Epstein, 1962; Clayton, 1993; Magna et al., 2017).

## 2 Aims of the research

The main aim of this thesis is to present a thorough study of the structural features of tektites and tektite-like glasses and gain more information concerning the traces of extraterrestrial matter in these materials from different geographic areas. I have focused mainly on the study of tektite-like glasses from the Zhamanshin impact structure, moldavites, and the Australasian Muong Nong- and splash-form-type tektites from Laos. In addition I have studied available source material, which could be a source of tektites and tektite-like glasses.

The thesis is divided into three principal parts respecting the geographical origin of individual studied materials.

*Part I: For tektite-like glasses from the Zhamanshin impact structure I have aimed to*

- (i) Describe the internal microstructure of assorted splash-form glasses.
- (ii) Evaluate the distribution of major, minor or trace element compositions in miscellaneous studied glasses.
- (iii) Determine the concentration of Os isotope ratios and contents of highly siderophile elements in chemically different splash-form glasses – based on the data obtained with an attempt to determine or derive the type of projectile.

*Part II: Topics covered in the study of moldavites included*

- (i) The study of near-surface sediments of the Upper Freshwater Molasse of Miocene age and comparing these results with the chemical composition of moldavites.
- (ii) Investigation of osmium and highly siderophile elements (HSE) behavior during moldavite formation.
- (iii) Identification of moldavite found in the Cenozoic sediments in Lower Silesia in Poland. Determination if Polish moldavites are similar to other sub-strewn fields of moldavites or whether these moldavites represent a new separate sub-strewn field.

*Part III: In Australasian Muong Nong-type tektites, the principal goals included*

- (i) Mapping out the occurrence of inclusions or other unusual microstructure phenomena within the Muong Nong-type tektites. Where technically feasible, attempt to determine the crystal structure of inclusions. Check for the potential chemical signature from an extraterrestrial projectile.
- (ii) Study of the structural features and chemical composition (optical, SEM/BSE, EDS, EBSD, EPMA, LA-ICP-MS) of Muong Nong-type tektites (inclusions, heterogeneity, the occurrence of vesicles) to define their microstructure. Characterization of the microstructure of Australasian tektites was important to choose suitable samples for subsequent analysis (e.g., triple oxygen isotope, Re–Os, Sr–Nd–Pb isotope systems, HSE contents)

In the last chapter, I aimed at the glass microstructures mutual comparison, discussion of contents of extraterrestrial components in them and eventually the determination of the potential projectile type.



### 3 Methodology

A concerted and multi-analytical approach has been adopted. Various analytical techniques and equipment were used for the study of the microstructure of samples (e.g., electron microscopes with various types of detectors). All samples were characterized visually and studied in detail using an optical stereomicroscope and polarization microscope. Quantitative determinations were performed by an electron probe microanalyzer (EPMA) equipped with four wavelength-dispersive X-ray spectrometers (WDS). Qualitative and semi-quantitative chemical analysis, line scanning, and fast elemental mapping were carried out by scanning electron microscopy with an X-ray spectral microanalysis (SEM/EDS). For imaging and distinguishing different phases and heterogeneities, electron microscopy with a backscattered electron detector (SEM/BSE) was used. Sample surface topography was imaged using a secondary electron detector (SEM/SE). Electron backscatter diffraction detector (SEM/EBSD) was the method of choice for structural characterization of small unknown mineral phases. Cathodoluminescence detector (SEM/CL) determined the internal zonal structure. Raman microspectrometry (RS) was utilized to identify individual phases in inclusions. The powder X-ray diffraction (PXRD) was also used for the identification of crystalline phases.

Geochemical methods have been applied to determine the presence/absence of the traces of an extraterrestrial component. To specify trace and rare earth element compositions, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used. The concentrations of highly siderophile elements (HSE) and Re–Os, Cr, and triple-oxygen isotope systematics were also studied.

The details of the methods, techniques, and instrumentations are given in the relevant attached papers in Appendix.



## 4 Results and discussion

### 4.1 Part I: Glasses from the Zhamanshin impact structure

#### *Article I*

**IF 4.609**      **Jonášová Š.**, Ackerman L., Žák K., Skála R., Ďurišová J., Deutsch A. and Magna T. (2016) Geochemistry of impact glasses and target rocks from the Zhamanshin impact structure, Kazakhstan: Implications for mixing of target and impactor matter. *Geochimica et Cosmochimica Acta* **190**, 239–264.

#### *Article II*

**IF 12.353**      Magna T., Žák K., Pack A., Moynier F., Mougél B., Peters S., Skála R., **Jonášová Š.**, Mizera J. and Řanda Z. (2017) Zhamanshin astrobleme provides evidence for carbonaceous chondrite and post-impact exchange between ejecta and Earth's atmosphere. *Nature Communication* **8**: 227, 1–8.

These two articles describe the study of the structural features of the Zhamanshin impact glasses and provide, for the first time, more information concerning the contents or traces of the extraterrestrial matter in these impact glasses. For the Zhamanshin impact structure, very chemically variable and differently shaped impact glasses are typical. These include basic splash-forms (typically 53–56 wt.% SiO<sub>2</sub>), acidic types (irghizites; typically 69–76 wt.% SiO<sub>2</sub>), newly identified rarely-occurring highly heterogeneous splash-form composites, and larger irregularly-shaped fragments and blocks of impact glass (zhamanshinites) (e.g., Florenski, 1977; Fredriksson et al., 1977; Heide and Schmidt, 1978; Florenskii and Dabizha, 1980; Glass et al., 1983).

These glasses were formed by different processes during the impact event and their target rocks are variable due to the progressive penetration of the projectile into the target materials. Irghizites originated from the uppermost target layers (poorly consolidated sediments, rich in quartz and clay minerals). Parent materials of irghizites were shocked at high pressure and melted at the highest extreme post-shock temperature and ejected at velocities of several km.s<sup>-1</sup>, reaching high altitudes above ground in the ejecta plume. The basic splash-forms were formed from the melting of deeper layers (Upper Paleozoic volcano-sedimentary lithologies – andesite, diabase, and their tuffitic analogs). Basic

splash-forms have higher volatile element contents, indicating lower temperatures than experienced by irghizites and composite splash-forms (Jonášová et al., 2016).

Study of the structural features provided new insights into the inner structures of the above-mentioned types of glasses. Irghizites were formed by coalescence of up to 1 mm large glass droplets with irregular internal coloring and dark rims caused by changes in major element composition. In contrast, the internal structure of basic splash-forms is usually fluidal and generally more homogeneous. The inner structure of composite sample IR 7 is inhomogeneous with both small and large bubbles, and the presence of common lechatelierite inclusions. Composite splash-form features more translucent brown color than irghizites and basic splash-form (Jonášová et al., 2016).

However, in all types of studied glasses several small inclusions were identified: quartz or transition of quartz to melt (Fig. 2 a) or lechatelierite (Fig. 2 b), Ni–Fe–S alloy (Fig. 2 b), zircon (Fig. 2c), Fe-, Cr-, Ni- and Ti-bearing oxides (Fig. 2 d,e), K-feldspar (Fig. 2 f) and iron-bearing phases (Fig. 2 g-l). Images Fig. 2 k-l show transformation from hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ), which can be used as an indicator of redox conditions during the formation of glasses from ZIS. The iron-bearing phases, which are by far the most common type of inclusions, are visibly cracked or show a partial melting or re-crystallization which processes may provide evidence of the degree of shock transformations.

Additional notable finding includes a white inclusion (Fig. 3 a-f), which was discovered during the preparation of the thin-sections. The secondary origin of this inclusion was ruled out. Raman microscopy and XRD identified the inclusion as bassanite (monoclinic  $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ ). How the inclusion found itself inside the vesicle remains unexplained. Probably during the formation of irghizites from the target rocks, several gaseous phases were trapped inside the newly formed tektite and the space in the bubble allowed subsequent recrystallization.

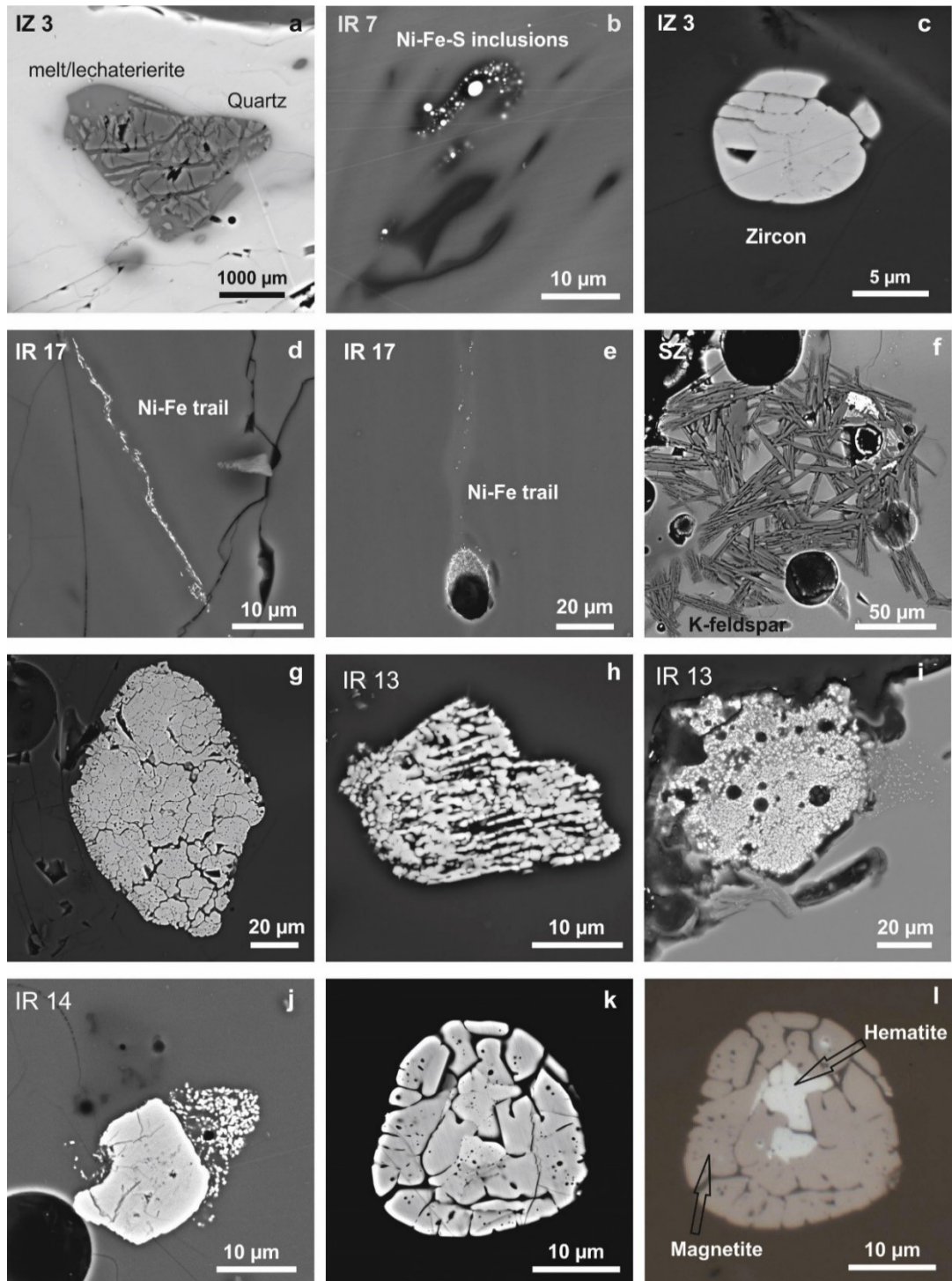


Figure 2: Photographs of (a) quartz-melt transition, (b) Ni-Fe-S inclusions, (c) zircon, (d,e) Fe-Cr-Ni-Ti bearing trail, (f) K-feldspar inclusions, (g-l) different types and shapes of Fe-bearing inclusions, (k,l) hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) transformation. (a-k) SEM/BSE, (l) optical image in reflected light.

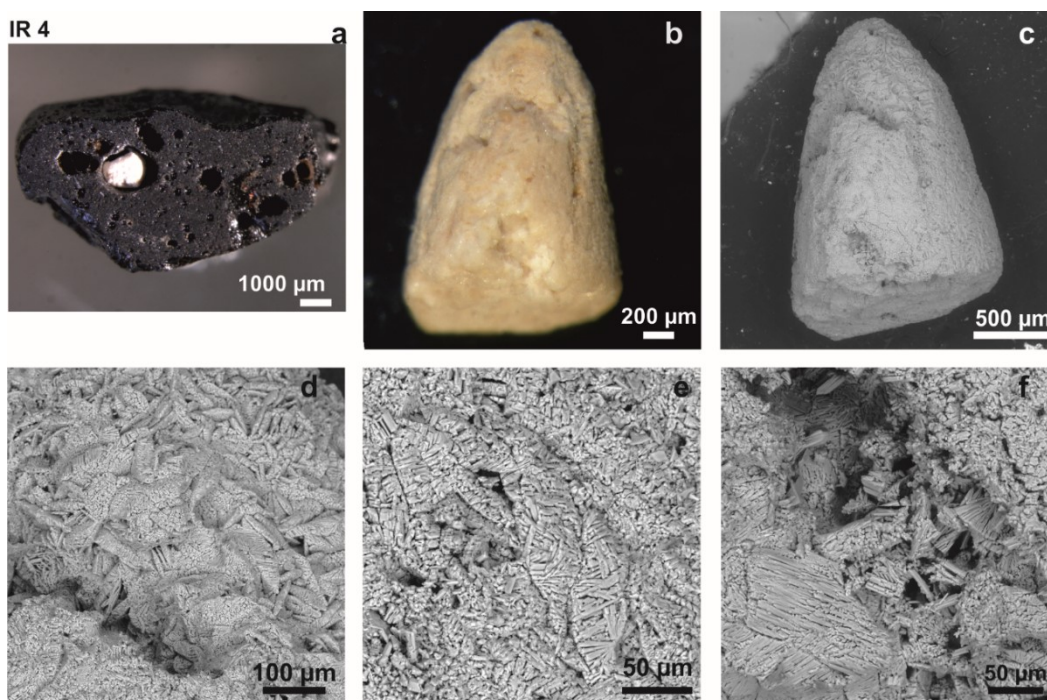


Figure 3: White inclusion found in irghizite. Photographs (a) Inclusion inside irghizite. (b, c) Photographs of inclusion taken using optical microscopy and backscattered electron imaging (BSE). (d -f) Detail view of inclusion surface in BSE.

The geochemical data as PGE, HSE, triple oxygen isotopes and chromium isotope signatures were used to yield more information concerning the contents and character of the extraterrestrial matter.

In Jonášová et al. (2016), we determined that the projectile could have been a carbonaceous chondrite (excluding CI group) due to triple oxygen isotopic constraints. But the next study involving chromium isotopes (Magna et al., 2017) refuted this exclusion and, conversely, suggested a CI-like chondrite impactor as the best match. The procedure for determining or excluding individual meteorite groups is shown in Fig. 4. HSE elements were probably affected by volatilization and condensation processes during the impact therefore these datasets do not constrain the projectile type unambiguously.

**Simplified Meteorite Classification for Constraints on the Nature of the Projectile of ZIS**

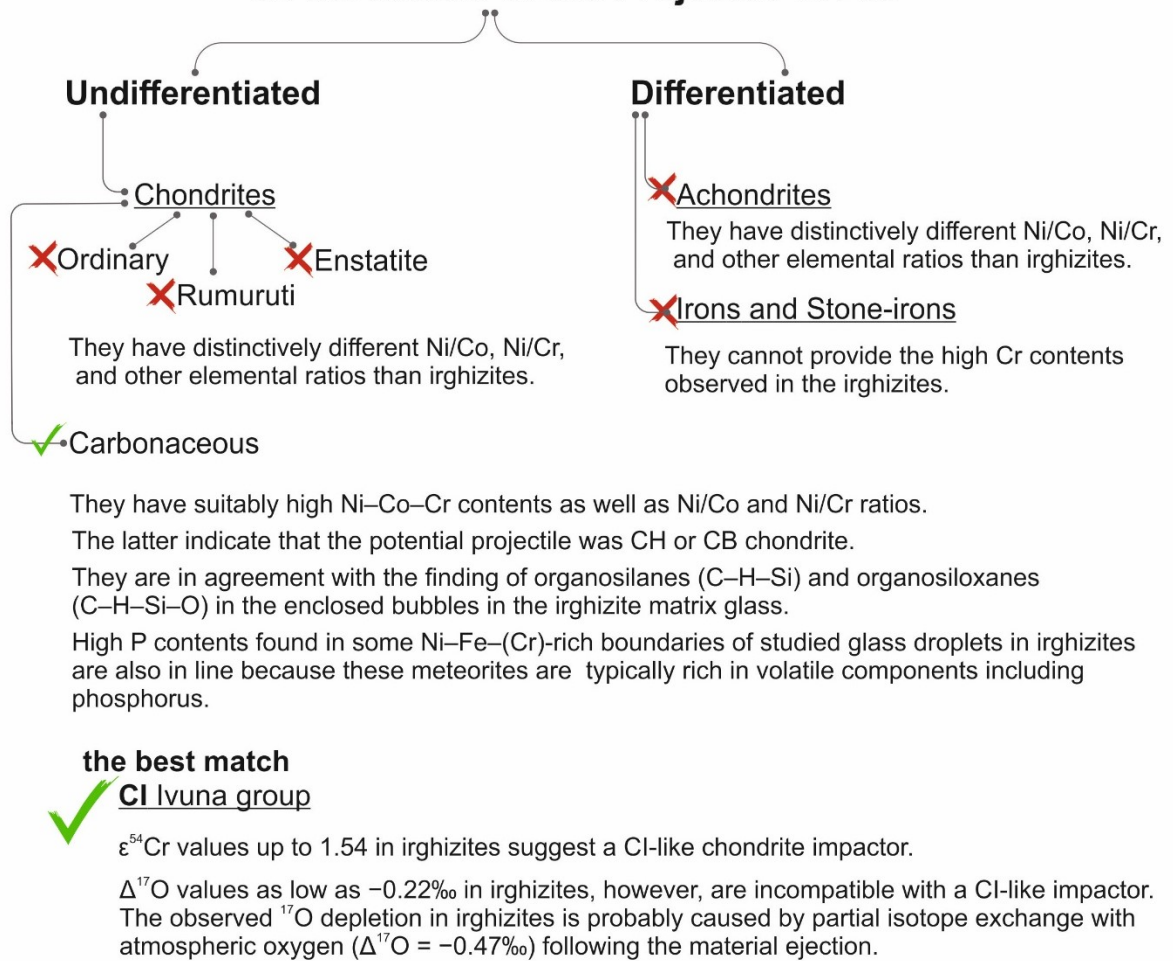


Figure 4: Constraints on the nature of the projectile of ZIS

## 4.2 Part II: Moldavite tektites

### *Article III*

**IF 4.609** Žák K., Skála R., Řanda Z., Mizera J., Heissig K., Ackerman L., Ďurišová J., Jonášová Š., Kameník J. and Magna T. (2016) Chemistry of Tertiary sediments in the surroundings of the Ries impact structure and moldavite formation revisited. *Geochimica et Cosmochimica Acta* **179**, 287–311.

### *Article IV*

**IF 4.690** Ackerman L., Magna T., Žák K., Skála R., Jonášová Š., Mizera J. and Řanda Z. (2017) The behavior of osmium and other siderophile elements during impacts: Insights from the Ries impact structure and central European tektites. *Geochimica et Cosmochimica Acta* **210**, 59–70.

### *Article V*

**IF 0.609** Skála R., Jonášová Š., Žák K., Ďurišová J., Brachaniec T. and Magna T. (2016) New constraints on the Polish moldavite finds: a separate sub-strewn field of the central European tektite field or re-deposited materials? *Journal of Geosciences* **61**, 171–191.

Among important papers focused on moldavites and presented here is the contribution by Žák et al. (2016). It summarizes thorough chemical study of the Tertiary sediments collected at the Ries impact structure surroundings and the compositional data on selected moldavites. The data were collected by a suite of analytical methods and critically evaluated to exclude potentially deleterious values due to methodologic shortcomings (e.g., limited applicability of ICP-MS to determine trace contents of As, problematic results in determination of Zr, Hf, Ta and Nb after solving of samples and subsequent application of ICP-MS; Table 2 and Table 4 in the referenced paper indicate the used methodology). Chemical compositions of moldavites and sediments were then mutually compared. This comparison provided a guide to identify sediments most suited to produce tektite melt. Chemical data for such preselected set of sediments including sand, marls and clays were averaged. Subsequently averages for sediments representing the so-called Upper Freshwater



Molasse (Obere Süßwassermolasse, OSM) and moldavites were presented in the plot (Fig. 4 in Žák et al., 2016) to show depletion/enrichment of moldavites in comparison with the OSM sediments. The plot accentuates mostly marked enrichment in LILE (large-ion lithophile elements) and strong depletion in volatile elements. This trend indicates that available sedimentary suite does not match chemical composition of moldavites completely and an addition of further lithology(ies) and/or complex chemical processes in moldavite vapor/melt jet(s) are required. These processes are graphically outlined in Fig. 5 of Žák et al. (2016) where introduction of organic matter and interaction of melt droplets later coalescing into larger moldavites bodies are discussed.

In the past, several studies aimed to characterize a projectile that excavated the Ries crater and ultimately produced the moldavites. Morgan et al. (1979) hypothesized that considering the chemical composition of shocked local rocks and impact glass in suevite and local lithologies the most plausible candidate for the Ries impactor is a sort of anomalous aubrite. It should be noted that though sought for, no meteoritic addition has been found in moldavite glass. Pernicka and Wasson (1987) and Schmidt and Pernicka (1994) concluded from studies of suevite from the research borehole Nördlingen 1973 and amphibolite below the crater floor, respectively, that chemical data provide no clear evidence for impactor type determination. Later, Reimold et al. (2013) analyzed suevite samples from the SUBO 18 borehole near Enkingen and found PGE enrichment compatible with ca 0.1-0.2 % addition of chondritic component. PGE systematics did not allow complete chondrite identification. In continuation of the study of moldavites and their relation to potential Miocene sedimentary precursors by Žák et al. (2016), HSE elements and osmium isotope systematics have been determined for a suite of sediments, suevite, shocked basement and South Bohemian and Moravian moldavites (Ackerman et al., 2017). Low osmium contents in both sediments and moldavites substantiate their genetic relationship. Contrary to results published earlier, no obvious evidence for a specific meteoritic component has been noted neither in suevites nor shocked country rocks. In moldavites, a meteoritic component can be identified through mutual relationships between Os, Ir, Ni, and  $^{187}\text{Os}/^{188}\text{Os}$  though it could not be characterized in more detail nor quantified (Ackerman et al., 2017).

Traditionally, moldavites have been described from South Bohemia and Western Moravia. Later, new sub-strewn fields have been identified in Lusatia in Germany, in Horn area in Austria and in the Cheb Basin (Trnka and Houzar, 2002 and references therein).

More recently, Brachaniec et al. (2014) found tiny fragments of moldavites in two sandpits close to Wrocław (Poland), which significantly extends the entire CET strewn field and shifts its perimeter up to ~475 km from the center of the Ries structure. Later, Brachaniec et al. (2014) identified additional moldavite fragments from sandpits along German-Polish border close to Gozdnica. Since at the time of description of these moldavite finds in Poland little has been known about their chemical composition, one piece of moldavite collected in the North Stanisław sandpit near Wrocław was chemically characterized.

The chemical compositions (major and trace element) of this Polish moldavite is indistinguishable from general compositional trends of moldavites from other sub-strewn fields. The internal structure of the studied moldavite showed marked chemical heterogeneity. Observations of the microstructure (e.g., using the SEM/BSE/EDS/CL) revealed lechatelierite grains, compositionally different schlieren, and the presence high-Ca–Mg schlieren and bubbles of different sizes. The high-Ca–Mg schlieren is a rather unique group - such a composition is identified in only several samples of South Bohemian moldavites (Skála et al., 2016). After considering all aspects, we concluded that the Polish moldavites were not re-deposited from the Lusatian sub-strewn field by fluvial transport in the Late Miocene as suggested by Brachaniec et al. (2014, 2015), however, they represent fluvially re-deposited material from a new as-yet-unknown sub-strewn field located south of the place of their present-day occurrence (Skála et al., 2016).

### 4.3 Part III: Australasian tektites

#### *Article VI*

**IF 2.631** Křížová Š., Skála R., Halodová P., Žák K. and Ackerman L. (2019) Near end-member shenzhuangite, NiFeS<sub>2</sub>, found in Muong Nong-type tektites from Laos. *American Mineralogist* **104**, 1165–1172.

#### *Article VII*

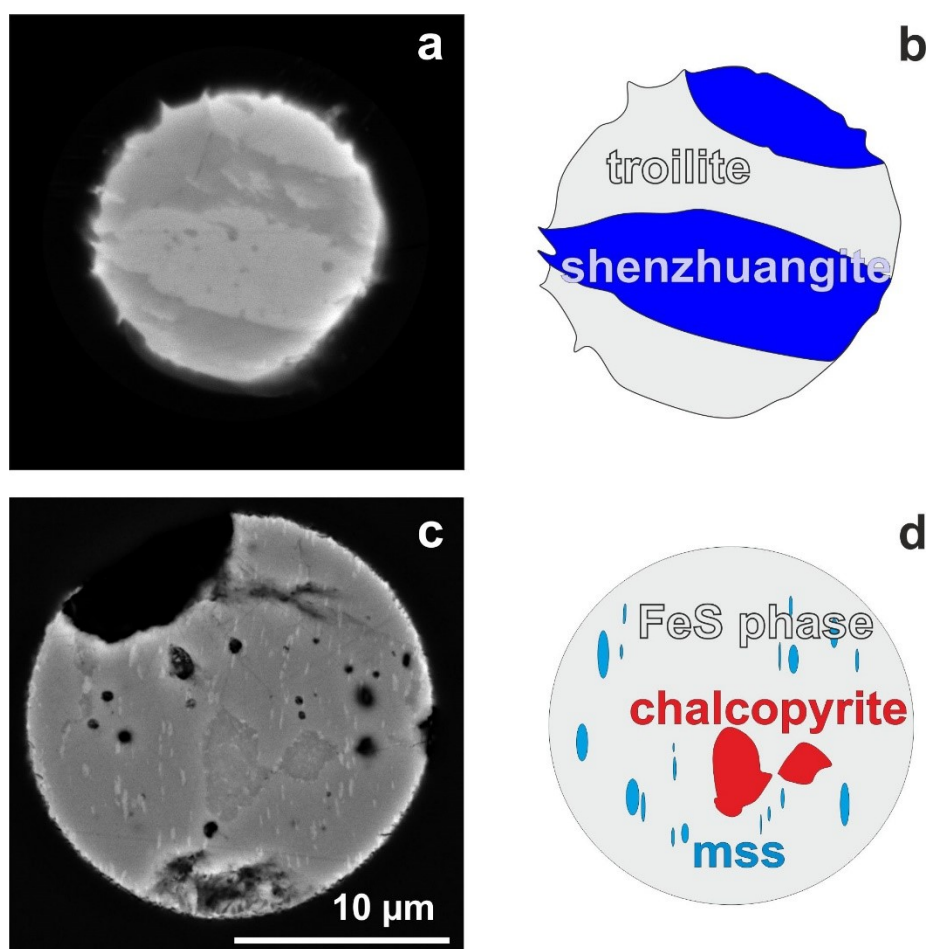
**IF 4.258** Ackerman L., Skála R., Křížová Š., Žák K. and Magna T. (2019) The quest for an extraterrestrial component in Muong Nong-type and splash-form Australasian tektites from Laos using highly siderophile elements and Re–Os isotope systematics. *Geochimica et Cosmochimica Acta* **252**, 179–189.

#### *Article VIII*

**IF 2.318** Žák K., Skála R., Pack A., Ackerman L. and Křížová Š. (2019) Triple oxygen isotope composition of Australasian tektites. *Meteoritics & Planetary Science* **54**, 1167–1181.

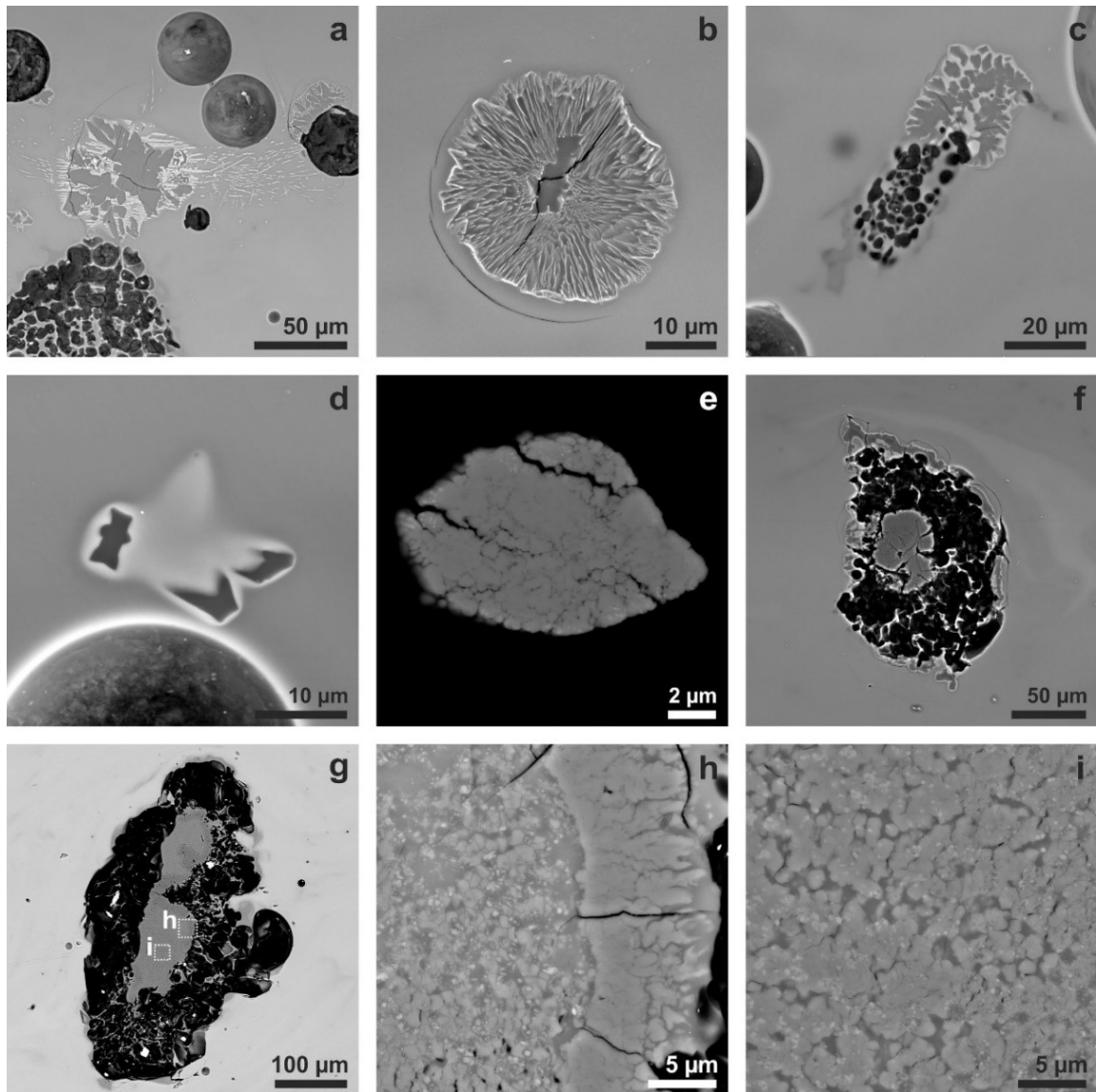
Numerous solid-state inclusions and quenched melt flow/coalescence phenomena can be detected in the microstructure of AAT, which require further detailed studies. I focused on sulfide inclusions, that were studied in Muong Nong-type AAT in detail for the first time ever and the results are given in Křížová et al. (2019) with part of compositional data not yet published. Sulfide inclusions with a diameter <5-20µm occur randomly in portions containing numerous small vesicles. Detailed identification and mineralogical, study of the structural features, and chemical characterization of phases in heterogeneous sulfide globules have been performed. The sulfide inclusions can be divided into two groups following the results of combined optical microscopy, BSE, EDS, WDS, EBSD, Raman microspectroscopy and LA-ICP-MS analyses. The Type 1 inclusions are composed of shenzhuangite (NiFeS<sub>2</sub>) and troilite (FeS). Shenzhuangite is a rare mineral, which was so far found only in the Suizhou L6 chondrite (Bindi and Xie, 2018). The article of Křížová et al. (2019) provides a comprehensive characterization of inclusions of type 1. The Type 2

inclusions are composed of chalcopyrite ( $\text{CuFeS}_2$ ), not yet identified FeS phase and monosulfide solid solution (mss). In general, the globules can be derived from a wide range of the assumed target rocks or can represent an extraterrestrial component addition from a projectile. From combined occurrence of shenzhuangite and troilite, paralleled by elevated contents of Co, Cu, Pt, and Pd it is likely that the sulfide globules carry an addition of meteoritic component. A plausible scenario for the origin of sulfides is that, under high temperature and pressure conditions at extremely low oxygen fugacities (i.e., in highly reducing environment) followed by subsequent rapid cooling, the sulfur-rich droplets of melt were separated from the silicate-rich melt to form an immiscible sulfide melt that was immediately encapsulated in a silicate glass matrix.



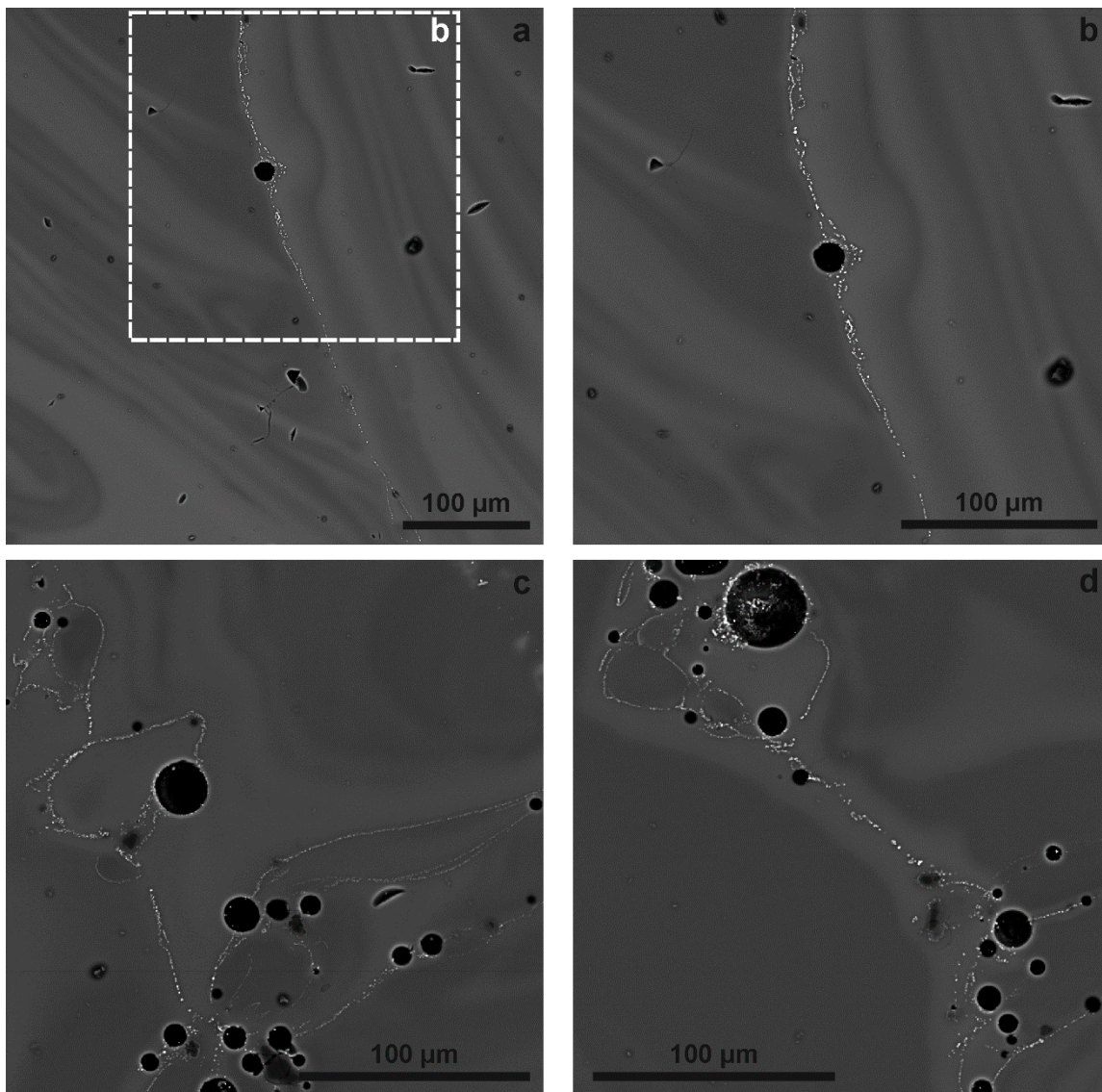
*Figure 5: Graphical representation of sulfide inclusions of type 1 (a, b) and type 2 (c, d), found in MNAAT from Laos.*

Next to sulfide globules, many MN AAT contain further inclusions of variable shapes, structures and compositions. Due to the complexity of this issue, I do not deal with these discoveries in my PhD thesis in detail. Figure 6 summarizes selected type of inclusions I noted when studying MN AAT from Laos.



*Figure 6: Backscattered electron images of different type inclusions found in MN AAT from Laos. (a) angular lechatelierite inclusion overgrown by a skeletal aggregate of Ca-Mg-Fe silicate; (b) radial aggregate of unknown silicate crystals; (c) complex frothy lechatelierite inclusion intergrown with an aggregate of lechatelierite and unknown silicate; (d) two-phase inclusion consisting of lechatelierite (dark) and unknown silicate or silicate glass containing Mg, Fe, Ca; (e) granular, most probably neoformed, zircon in association with nanometer-sized ZrO<sub>2</sub> domains; (f) frothy lechatelierite; (g,h,i) intimate inergrowth of quartz and coesite in association with silica glass surrounded by a froth lechatelierite layer.*

Microscopic studies (SEM/EDS/BSE) of some MN type tektite samples revealed the coalescence of small glass patches that may have once been droplets. These objects are often rimmed by shells of melts of slightly different chemical composition (Fig. 7). The same phenomenon has been noticed in irghizites before (Jonášová et al., 2016). Possibly, this feature may provide a closer insight into the Muong Nong-type tektite formation during the impact process. In some cases, the boundaries between glass droplets or patches are decorated by trails consisting of tiny grains of oxides or sulfides (Fig. 1a-d).



*Figure 7: Deformed small glass droplets forming irregular patches that are rimmed by melts of slightly different chemical composition and/or occasionally also trails consisting of tiny grains of oxides or sulfides. In addition, marked chemical variability is conspicuous.*

The HSE contents, Re–Os isotopic and triple oxygen isotope systematics for well-characterized individual specimens of Australasian tektites including both MN and SF were determined in attempt to detect the potential extraterrestrial component. The optically different zones (dark and light) were studied in MN AAT separately and they have highly variable HSE systematics and Re–Os isotopic compositions suggesting mingling of crust-derived (siderophile element-poor) and extraterrestrial (siderophile element-rich) materials. However, the combined HSE concentration and Os isotopic systematics data do not conform to the direct involvement of common upper continental crustal materials. It suggests that the sea water could have been involved in the formation of Australasian tektites, which could explain the evaporative loss of Os from the overheated tektite melt (Ackerman et al., 2019). Elevated contents of halogens (e.g., Koeberl, 1992; Meisel et al., 1992) further support a saline character of the pore water in the target rock. The triple oxygen isotope data fit the range of those typical for terrestrial crustal rocks and do not attest for mass-independent oxygen isotope fractionation (from impactor or from exchange with atmospheric oxygen) (Žák et al., 2019).

#### **4.4 Comparison of microstructures and contents of extraterrestrial components in studied glasses**

The microstructures observed in proximal impact glasses from the ZIS, distal impact glasses from the Central European tektite strewn field and Laotian part of the Australasian tektite strewn fields differ mutually.

Three types of tektite-like glasses from the ZIS were studied: irghizites, basic splash-forms and composite splash-form. Although they represent products of a single impact event, their microstructures differ from each other markedly. Clearly, these glasses not only originated from variable precursors but they faced different conditions under which formed.

In moldavites, common lechatelierite particles and scarce relict mineral inclusions point to silica-rich sedimentary source rocks. To date, no unequivocally identified metal- or sulfide-bearing inclusions have been found in moldavites, or other chemical identifiers that would attest to the extraterrestrial component.

The presence of sulfide-bearing spherule inclusions in MN AAT tektite glass collected in Laos is of utmost importance. These objects either could have been derived from minerals present in the pre-existing target rock or they may have formed from a

projectile matter. In the latter case, sulfide phases of a meteorite turned to a melt that was immiscible in silicate tektite melt. These immiscible sulfide blebs finally formed spherical objects now preserved as sulfide-bearing inclusions.

The identification of an admixture of extraterrestrial material into impact glasses and the determination of the type of meteorite involved represent one of the most intriguing tasks. In general, the verification of an extraterrestrial component is not straightforward, as vapor fractionation during the impact, as well as post-impact fractionation in the melt or hydrothermal mobilization, may lead to changes in the interelement ratios. Among the studied impact glasses, the type of projectile could be specified in more detail only for tektite-like glasses from the ZIS. For moldavites and AAT, it was not possible to specify the type of projectile in more detail based on the measured data. Range of measured data sets of tektite-like glasses from the ZIS, moldavites and AATs are given in Table 1.

Table 1: Comparisons of data delineating possible extraterrestrial contribution in studied glasses

	ZIS		Moldavites	AATs	
	Irghizites	Basic splash-forms		MNT tektites	Splash-forms
Ni/Cr	5.2–8.0	0.5–2.3	0.3–0.8	0.4–1.3	0.9–1.4
Ni/Co	13.2–19.4	0.5–3.9	1.1–3.4	2.0–8.3	5.5–8.8
Os/Ir	0.01–0.267	0.01–0.41	0.04–1.00	0.08–2.17	0.07–7.17
$^{187}\text{Re}/^{188}\text{Os}$	7.7–34.1	up to 0.82	58–86	3.2–73	11
$^{187}\text{Os}/^{188}\text{Os}$	0.12–0.15	0.13–0.17	0.12–0.16	0.13–0.68	0.13–0.28
$\delta^{18}\text{O}$ (‰)	11.85–14.42	8.01–9.18	9.44–12.57	8.71–11.61	10.03–11.14
$\Delta^{17}\text{O}$ (‰)	-0.22–(-0.14)	-0.1–(-0.07)	-0.11–(-0.7)	-0.098–(-0.069)	-0.080–(-0.068)
$\varepsilon^{54}\text{Cr}$	up to 1.54	n.m.	0.09	n.m.	n.m.

n.m. – not measured



## 5 Conclusions

The objectives of this project included (i) the study of the microstructure of tektites from the Australasian and Central European strewn fields and tektite-like glasses of the Zhamanshin impact structure, and (ii) a quest for potential content of an extraterrestrial admixture being incorporated in the glass structure or trapped as inclusions. Further, once identified in the Zhamanshin impact structure glasses, the character of such an extraterrestrial component was tested. To accomplish these goals the PhD project has benefited from a multidisciplinary qualitative and quantitative approach.

*The following conclusions can be drawn from this study.*

### (1) Tektite-like glasses from ZIS

- Rarely-occurring highly heterogeneous splash-form composites, which chemically differ from in the literature previously described irghizites and basic splash-forms were identified as a new type of tektite-like glassy objects in the ZIS
- Study of the structural features provided new insights into the inner structures of the above-mentioned types of tektite-like glasses.
- In iron-bearing oxide phases, some important features were observed including:
  - Grains are visibly cracked or show a partial melting or re-crystallization, which processes may provide evidence of the degree of shock transformations,
  - The transformation from hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) was observed, which can be used as an indicator of redox conditions during the formation of glasses from the ZIS.
- Unusual inclusion identified as bassanite (monoclinic  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) was found in one irghizite and might represent a back-reaction product of sulfate-bearing precursor with a silicate impact-generated melt
- For the first time, complex geochemical data (trace element contents including PGE and HSE, triple oxygen isotopes and chromium isotope signatures) suite allowed identification of an extraterrestrial matter admixture in these tektite-like glasses.
  - On the base of PGE and HSE contents and Re–Os and triple oxygen isotopes systematics, the potential projectile could have been a CH or CB carbonaceous chondrite.

- $\epsilon^{54}\text{Cr}$  values suggest a CI-like chondrite impactor questioning use of sole siderophile element ratios to identify projectile type in the case of metal-rich chondrite groups.

### (2) Moldavites (Central European tektites)

- Complex geochemical data comparison of moldavites and a suite of Miocene sedimentary rocks from the Ries crater area representing possible source rocks of the CETs supports the sedimentary parentage of moldavites, yet, simultaneously, postulates the process required to explain enrichment of volatile elements associated with depletion in refractory ones in moldavites.
- No meteoritic addition has been found either in suevites or in shocked country rocks.
- Moldavites contain extremely low contents of HSE with strongly fractionated HSE patterns. Yet, at the same time, moldavites show low  $^{187}\text{Os}/^{188}\text{Os}$  ratios ( $<0.163$ ) indicative of possible addition of impactor matter though it could not be either characterized in more detail or quantified.
- Chemical composition of one of a suite of moldavites collected near Wrocław (Poland) was measured to identify its alleged association with Lusatian sub-strewn field.
  - The moldavite cannot be associated with any of the known moldavite sub-strewn fields based on its chemical composition or structure unequivocally. Its redeposition from Lusatia is not substantiated from either a chemical or paleogeographic point of view.
  - The original place of deposition of these moldavites may be sought in the piedmont of Sudetic Mountains south of the place of their present-day occurrence.

### (3) MN/ SF AAT

- Two types of sulfide inclusions were found in MN AAT
  - Type 1 inclusions are composed of shenzhuangite (chalcopyrite-structured  $\text{NiFeS}_2$ ) and troilite (hexagonal stoichiometric  $\text{FeS}$ ).
  - Type 2 inclusions are composed of chalcopyrite ( $\text{CuFeS}_2$ ), not yet identified  $\text{FeS}$  phase and monosulfide solid solution (mss).

- Tentatively it is assumed that inclusions of type 1 are derived from a meteorite whereas type 2 represent reworked terrestrial material, though solid evidence for this conclusion is missing.
- MN AATs contain also other inclusions of variable shapes, structures and compositions. Due to the complexity of this issue, I do not deal with these discoveries in my PhD thesis in detail.
- Careful observation (SEM/BSE) revealed for the first time in AAT the coalescence of small glass droplets rimmed by shells of melts of slightly different chemical compositions.
- Collected compositional data sets (PGE, HSE, Os isotope systematics, and triple oxygen isotope data) do not indicate that AA tektites might be modified either by the projectile matter admixture or by an interaction with the atmosphere. Therefore, the projectile type cannot be closer specified.

#### **(4) Generalized conclusions on projectile fingerprinting in impact glasses**

- Unequivocal identification of extraterrestrial material presence in tektites and tektite-like glasses is possible when high enough contents of (highly) siderophile elements (Ni, Co, Cr, HSE) are present to allow meaningful calculation of diagnostic parameters. Next to sole ratios of these element contents, their higher contents may allow determination of isotopic compositions of, e.g., osmium or chromium, to shed light on character of a projectile in more detail.
- Although there is a large database of siderophile element ratios in different meteorite group (Tagle and Berlin, 2008), their use may be limited for identification of particular meteorite group as exemplified in the case of the samples from the ZIS. Particularly, this is true for metal-rich chondrites like CH or CB groups.
- The use of HSE as well as Os isotopic systematics otherwise sensitive to meteorite type determination may be highly influenced by a pronounced fractionation or even a significant loss of HSE from tektite glass at its early formation stage.
- In general, determination of meteoritic component in tektites and tektite-like glasses suffers from a limited meteorite matter available to be incorporated to the glass. One should keep in mind that normally, tektite glass is formed at the very

beginning of the projectile contact with the Earth surface or even, in part, before actual contact occurs. Consequently, the volume of a projectile in contact with tektite parent sediments is very low if any depending on the character of the projectile, impact velocity and incidence angle. Under certain circumstances, it might happen that sediments meet just a bow shock wave in front of a projectile, which does not bring any solid projectile material to contribute to a tektite melt.

- Oxygen isotopes are unfortunately of limited use. To notice any meteoritic contribution, the admixture of a projectile would have to exceed several percent by weight, which is hardly possible once one considers ideas how the tektites had formed. On the contrary, oxygen isotope systematics is relatively sensitive in deciphering possible reactions of tektite melt/glass with other reservoirs as illustrated for the ZIS glasses.
- Presence and character of mineral inclusions in both AAT and glasses from the ZIS provide ambiguous answer to the questions whether a projectile material is included in these glasses. Most probably, the minerals found and their assemblages rather indicate the source material composition and conditions under which tektites have formed.
- In conclusion, the unambiguous indication of meteoritic component incorporation to impact glass has been observed among studied samples solely in certain irghizites. These tektite-like glasses found in the crater Zhamanshin or on its raised rim might be interpreted as fall-back ejecta of almost vertical impact. Possibly, such a geometry promotes incorporation of much higher amount of projectile material into ejecta compared to relatively inclined impact angles involved in actual tektite-forming events.

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## 6 Appendices

- I. **Jonášová Š.**, Ackerman L., Žák K., Skála R., Ďurišová J., Deutsch A. and Magna T. (2016) Geochemistry of impact glasses and target rocks from the Zhamanshin impact structure, Kazakhstan: Implications for mixing of target and impactor matter. *Geochimica et Cosmochimica Acta* **190**, 239–264.
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- IV. Ackerman L., Magna T., Žák K., Skála R., **Jonášová Š.**, Mizera J. and Řanda Z. (2017) The behavior of osmium and other siderophile elements during impacts: Insights from the Ries impact structure and central European tektites. *Geochimica et Cosmochimica Acta* **210**, 59–70.
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- VIII. Žák K., Skála R., Pack A., Ackerman L. and **Křížová Š.** (2019) Triple oxygen isotope composition of Australasian tektites. *Meteoritics & Planetary Science* **54**, 1167–1181.