

BONES, ROCKS, AND FLAMES:

Mineralogy and petrology of slags and cremated bones from ritual immolation sites in Tyrol

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Impetus for these investigations:

•Slag samples from an archaeological site in Oetz.

•Petrology of these slags as examples of pyrometamorphic rocks.

•Close collaboration between mineralogy/petrology and archaeology in the frame of the research center HiMAT.

•HiMAT stands for: The history of Mining in the Tyrol and Adjacent Areas.



Question:

Is it possible to find **mineralogical** evidence for fire/bone/rock interactions at ritual immolation sites?



Research history



Research on ritual immolation sites in the Alps started in 1966 by a paper by Werner Krämer.

He describes: ... where masses of calcinated bones allow the interpretation of ritual immolation....

...as well as the occurrence of large masses of ceramic fragments which can also be interpreted as sacrifical offerings....

For the **first time** these sites were considered from an archaeological standpoint as a group of their own.



His research focussed on the ritual immolation site at the **Schlern** in South Tyrol. This site is one of the **most impressive ritual immolation sites** in the Eastern Alps!



Steiner (2013)



Structure of this talk

- **1. Overview** of ritual immolation sites in the western part of the Eastern Alps.
- **2. Mineralogical/petrological investigations** of slags from two ritual immolation sites as well as on calcinated bones from two sites.
- **3. Experimental investigations on pyrometamorphism** of rocks and minerals and comparison to the slags from ritual immolation sites.
- 4. Experimental investigations of bone-rock interactions.
- 5. Discussion: the relevance of P-bearing phases in pyrometamorphic slags.
- 6. Conclusions



Overview of ritual immolation sites in the western part of the Eastern Alps



Ritual immolation sites in the Eastern Alps: Steiner (2013)

From when on? Beginning roughly in the Early Bronze Age occasionally lasts until the Roman period.

Who did it? Farming populations.

Why did they do it? Sacrifices for the gods for good harvests and herds.

What was sacrified? In the mountains goats and sheeps were sacrified in the valleys cows, pigs, deer etc. Usually skulls and extremities of the animals were sacrified.

Where did this take place? In the Bronze Age in isolated sites, in the Iron Age in the vicinity of dwellings.



Ritual immolation activities coincide with:

Increasing populations and henceIncreasing farming

from the Middle Bronze Age on.

What is the idea behind it?

Fire is considered to have **cleansing properties**. The so "cleansed" sacrifice is transferred to the gods **via smoke**.



What are the characteristics of alpine ritual immolation sites?

Not always easy to define!

- •Exposed position
- •Ash layers
- •Altars
- Calcinated bones
- •Bone deposits
- Ceramic fragments and other sacrified goods
- Pyrometamorphic slags



Exposed position



In the western part of the Eastern Alps (S-Bavaria to S-Tyrol) ca. **200 known ritual immolation sites** exist. Shown here is only a selection from Tyrol.





Many of them can be found on **exposed positions**.



Schlern/Seis

Steiner (2013)

Goldbichl/Igls

Tomedi (2013)



Ash layers



These ash layers vary in thickness. **Stratification occurs**





(1996) St. Walburg/Ulten

Steiner (2010)



Stratifications imply frequent re-use! This is an important criterium!



Tschurtschenthaler (1996)

Pillerhöhe



Altars



What do altars look like? They are circular structures made from rocks from the vicinity!



Links oben: Steinaltar *URL: //www.goldbichl.at/goldbichl%20fuer%20schuele.pdf* Rechts oben: *Steinaltar aus Ulten, Südtirol Gleirscher et al. (2002)*





Very often **several altars** occur!







St. Walburg/Ulten



Calcinated bone fragments



This is one of the **most characteristic and visible features** of ritual immolation sites!



Schlern/Seis

Steiner (2010)

Scheibenstuhl/Nenzing Wink & Kaufer (2013)





Schluderns

Steiner (2010)

Masses of small calcinated bone fragments occur.



St. Walburg/Ulten



Most bone fragments are either from **the skulls or the extremities** of the animals.





Bone deposits



In the **vicinity** of some sites, **bone deposits** occur. This indicates **ritual cleansing** of the site after the immolation process.





Ceramic fragments and other sacrified goods



Frequently ceramic fragments and metal objects can be found!





Pyrometamorphic slags



Depending on the rock type: **pyrometamorphic** slags occur sometimes.



Tropper et al. (2004)



Steiner (2010)



Goldbichl/Igls



Mineralogical/petrological investigations of pyrometamorphic slags from two ritual immolation sites in Tirol



- ➢ Mineralogical/petrological investigations allow putting constraints on firing temperatures as well the O₂-availability in the fire (fO_2). This information is based upon the occurrence of newly-formed phases.
- Which new high-temperature phases form?
- > Are they **diagnostic for the firing process**?
- > Do P-bearing phases occur and if are they diagnostic?

> What are the **temperature constraints** based on **calcinated bones**?



Pyrometamorphic slags from Oetz





Tropper et al. (2004)

This site was active during the **late La-Tène Time** (500 – 15 v. Chr.). It is located on **top of a small hill** outside of Oetz. Large amounts **ceramic fragments and animal bones** (sheep, goat, cow) were found.

Slagging occurs only on the surface of the orthogneiss rocks.



The mineral assemblage of the protolith orthoneisses is:

biotite + plagioclase + K-feldspar + muscovite + quartz.

The high-*T* mineral assemblage is:

P-bearing olivine + whitlockite + anorthite + glass.



This is a highly unusual P-rich mineral assemblage!

Tropper et al. (2004)



Olivines are mineralogically interesting: **high P-contents**!



Mineral chemistry shows that olivine **contains P (max. 9 wt.% P_2O_5)**. This substitution affects Si contents and total sum of cations according to the following vector: Tropper et al. (2004)

 $2P+(\square)M_{1,2} \leftrightarrow 2Si+(Mg,Fe)M_{1,2}$



Pyrometamorphic slags from the Goldbichl/lgls


Highly exposed position near Innsbruck

Tomedi (2012)











http://www.goldbichl.at/schule.html

This immolation site was active during the **Middle Bronze Age** (ca. 1900 - 1650 BC) and **the Late Iron Age** (ca. 500 - 15 BC).

Abundant bone and ceramic fragments as well as silex arrowheads were found.





Massive amounts of pyrometamorphic slags were found!



During **pyrometamorphism** the rock **Large degree of melting** changes its mineral assemblage: mineral reactions occur!



chlorite + muscovite + albite + quartz

Protolith rock assemblage:

Large degree of melting and mineral reactions occur! Rock changes texture and mineralogy. Former chlorite domain:

olivine + spinel + anorthite





In some localized areas P-rich micro-domains occur!



Schneider et al. (2013)

- •In the vicinity of apatite.
- Olivine contains up to 23 wt.% P₂O₅!
 Stanfieldite (TCP, Ca₄Mg₅(PO₄)₆) occurs.
 Anorthite contains up to 2 wt. % P₂O₅!

This is also a highly unusual Prich mineral assemblage!



This P-rich olivine shows the highest P-contents found on Earth so far!



 $2P+(\square)M_{1,2} \leftrightarrow 2Si+(Mg,Fe)M_{1,2}$

Due to the high PO₄ contents, **significant changes** in the Raman spectra occur.



Rough temperature constraints based on phase diagrams in the system SiO_2 -FeO-Al₂O₃ only possible!



Coexisting olivine + spinel indicate at least T ≥1000-1100°C!



Part 2-1 and 2-2 Conclusions

- Formation of micro-domains in the pyrometamorphic slags.
- No textural and chemical equilibrium in the slags!
- Temperature of formation >1000-1100°C.
- Extremely high P-contents of olivine.
 - P-phase occurrence (whitlockite, stanfildite) is highly interesting!
 - Petrological results now need to be correlated with experimental and archaeological evidence!

Questions to be answered:

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- What are the P-phases telling us?
 - Can we verify these high temperatures experimentally?
 - What do these high temperatures mean archaeologically?



What can be learned from calcinated bones?



Calcination is a **thermal treatment process** in presence of air or oxygen applied to ores and other solid materials to bring about a **thermal decomposition**, phase transition, or removal of a volatile fraction.

The calcination process normally takes place **at temperatures below the melting point** of the product materials.

Calcinated bones form at fire temperatures of up to 600°C. Organic matter **(collagen)** burns off and anorganic materials such as **hydroxyl-apatite** remains.

In the course of this process the color of the bones changes.



Verbrennungs- stufe	Färbung der Knochenreste	entsprechender Temperaturwert	Bemerkungen/Zustand der Knochenreste
I	gelblichweiß	fellow bis 200°C	wie unverbrannter, frischer Knochen
	glasig	um 250-300°C	erste Schrumpfung durch Wasserverlust (ca. 2%)
н	braun	Brown um 300°C	Beginn des Austriebs organisch gebundenen Kohlenstoffs
	dunkelbraun schwarz	Black um 400°C	Verkohlung der organischen Knochensubstanz
111	grau blaugrau, taubenblau milchig hellgrau	Grey um 550 °C	Kompakta manchmal innen noch schwarz
IV	milchig weiß mattweiß kreideartig	White ab 650–700°C	kreidig samtige, abreibbare Oberfläche (»kalziniert«) Kompakta innen manchmal noch grau ab ca. 750 °C kontinuierlich stärkere Schrumpfung
v	altweiß schmutzigweiß	White ab ca. 800 °C	Knochen spröde, hart und fest (»versintert«) Auftreten typischer Hitzerisse je nach Bodenlagerung hellbeigefarben, weißlichgrau o ä
The colo	or of bones chan	iges!	maximale Schumpfung (25–30%), durchschnittlich 12%
		Wahl (1997)	Spongiosa manchmal gelblich-ockerfarben

6.000 S 400.0



Due to heating **shrinking in size** and **strong fragmentation of bones** occurs. Typical fractures form during the firing process.







Bitterlich (2012)

BSE image of fractures due to decrease in size.

International Journal of Medical Sciences (2012)



Many bone fragments were retrieved from the **bone deposit Weer-Stadlerhof**.

Age: 1600-1250 BC

One of the oldest bone deposits found so far!

The position of the **ritual immolation site** has **not been found** yet.





Archaeozoological results:

•60740 sieved fragments

•3.4% (ca. 2000 pieces) could be attributed to animal species
•52% sheep/goat, 18% cow and 30% pig

Most bones from skull as well as extremities





XRD investigations of calcinated bones: high-T studies



XRD patterns become **sharper with increasing temperature** due to better crystallization of apatite.



Crystallite size (nm)

Part 2-3

XRD investigations of calcinated bones: crystallite size measurements

Piga et al. (2008) Crystallite size (nm) as a function of T Average crystallite size of the hydroxylapatite mineral phase (1 $\AA = 10^{-10}$ m) (Piga et al.(2008) 18 min Temperature (°C) 0 min 60 min 60 min Not burned 18 min ¥. 0 min >1500 (1616) >1500 (2621) >1500 (1569) >1500 (2195) >1500(2950)T(°C)

Calibration based **on cremated human remains**. Not only *T* is important, the **duration of firing** is important as well!



Weer/Stadlerhof

Part 2-3

XRD investigations of calcinated bones: crystallite size measurements



Scheibenstuhl/Nenzing







Part 2-3 Conclusions

- Bone colour (white) indicates high temperatures.
- High temperature leads to sharp diffraction patterns due to apatite recrystallization.
- Firing of bones is a multi-step process (H₂O-loss, burning off organic matter, recrystallization) that can be easily monitored using DTA-TG.
 - But calcinated bones indicate lower temperatures (>650°C) than the slags (1000-1100°C)!



Part 3

Experimental investigations of pyrometamorphic slags



Fire temperatures

The temperature in a large wood fire is approximately 800°C. By using bellows or wind-driven air circulation up to 1300°C can be reached.

Pyrometamorphic processes lead to the formation of slags!



• Can we reproduce the observed high-T mineral assemblages in the lab?

• Are there diagnostic mineral assemblages for immolation sites?



Part 3: Conclusions

The experimental investigations allow inferences about firing temperatures and fO₂. As starting materials natural rocks from the vicinity of the immolation sites are used: <u>1st set of experiments</u>

By using high-T XRD and differential thermal analysis (DTA-TG) the high-T behavior of chlorite can be investigated and the reaction products and textures can be compared to the slags: <u>2nd set of experiments</u>

In order to understand the occurrence of P-bearing minerals in the slags bone-rock experiments were conducted: <u>3rd set of experiments</u>



1st set of experiments: Experimental melting of natural rocks



- Quartzphyllites heated up to 1100°C in a graphite crucible.
- Cooling with 100°C/h (t^{total} = 20h) down to 500°C.



Graphite crucible and rock before the experiments.

Rock samples after the experiments.



Observed petrography and mineral chemistry:



Textural micro-domains and mineral chemical variations could be reproduced extremely well.



Part 3-1: Conclusions

- > The use of **graphite crucibles** leads to highly efficient melting.
- > The **textures** could be **well reproduced**.
 - Mineral chemical variations could also be well reproduced.
 - Comparison with natural samples indicates temperatures >1100°C!
 - fO₂ must have been highly reducing (probably around QFM)!



2nd set of experiments: Experimental investigations of the high-*T* behavior of chlorite



T-dependent reaction history of chlorite can be reconstructed.



Siemens D5005

Experiments were done under oxidizing conditions!

≻High-T XRD

Allows in-situ monitoring of mineral reactions as a function of temperature.

- 300-1200°C
- Heating rate 0.5°C/s
- Duration: 6 days 18 h.

Use of chlorite with X_{Fe} = 0.46, similar to chlorite from the quartzphyllites.



At 900°C **spinel** forms and around at 1120°C **sapphirine** appears which is followed by cristobalite around 1140-1160°C.



DTA-TG: Chlorite

*X*_{Fe} = 0.46





>DTA-TG

>Energy changes associated with mineral reactions as a function of temperature can be monitored in-situ (DTA).

>Mass changes as а function of temperature be can monitored (= TG).

➢ Reducing Heatmosphere was used.

Table 25: shows the different dehydroxylation temperatures, the DTA signals, the phase assemblage at the end of the DTA and the phase assemblage and their appearance under 1 atmosphere using HTXRD.

T^{initial} - Dehyd.: Temperature of dehydroxylation of the brucite - interlayer Dehyd .: Temperature of dehydroxylation of the talc - interlayer

Dehyd .: Temperature at which the dehydroxylation is completed

	T ^{initial} - Dehyd.	T™ - Dehyd.	T ^{end} - Dehyd.	Endothermic Peaks	Exothermic Peaks	New phases (He-atm.)	New phases (1 atm. air) with HTXRD
CE, clinochlore X _{Fe} =0.11	497°C	726°C, 813°C	880°C	497°C 726°C	807°C	forsterite + spinel + enstatite	820*C forsterite 950*C spinel 1010*C enstatite
CD, X _{Fe} =0.46	507°C	740°C	812°C	507°C	725°C 1150°C	spinel + enstatite + cristobalite	900°C pleonaste 1120°C sapphirine 1140°C cristobalite
	l						
CC, X _{Fe} =0.62	493°C	623°C	765°C	493°C	719°C	spinel + enstatite + cordierite	
CA, chamosite X _{Fe} =0.89	360°C	472°C	700°C	400°C 483°C 1018°C 1088°C	707°C	melt / no phase analyses	900°C hematite 1100°C mullite 1160°C sapphirine + cristobalite

Schneider (2009)



Both methods allow to infer the following ideal chlorite breakdown reaction:

Mg-endmember clinochlor breakdown:

Clinochlore \rightarrow Forsterite + Enstatite + Spinel + $4H_2O$ Mg₅Al₂Si₃O₁₀(OH)₄ \rightarrow Mg₂SiO₄ + MgAl₂O₄ + 2MgSiO₃ + $4H_2O$

Comparison with a chlorite domain in the slags from the Goldbichl.

Reducing experiments are correct!



Observed mineral assemblage: olivine + orthopyroxene + spinel + melt.



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Part 3-2: Conclusions

- Mineral breakdown reactions can be monitored in-situ!
- ➤ Dehydration behavior of chlorite is complex (olivine \rightarrow spinel \rightarrow orthopyroxene).
- Chlorite has a high thermal stability. It completely disappears above 800°C.
 - The mineral assemblage from the reducing DTA (He-atmosphere) experiments at X_{Fe} = 0.46 can be observed in the slags.
 - The results also indicate T> 1100°C at the Goldbichl site.



Part 4

3rd set of experiments: Experimental investigations of bone-rock interactions



In the slags from Oetz and Goldbichl P-bearing phases (olivine, clinopyroxene) as well as phosphates occur.

The most prominent phosphates are whitlockite, $Ca_9(Mg,Fe)[PO_3OH|(PO_4)_6]$, and stanfieldite, $Ca_4(Mg, Fe^{2+}, Mn^{2+})_5(PO_4)_6$.

Is it possible to create these phases experimentally?

In order to identify diagnostic P-phases bone-rock experiments were conducted.



Part 4

Tropper et al. (2006): Bone-rock experiments using orthogneisses from Oetz.

Chicken bone layer on top of an orthogneiss cube.



1100°C experiment in graphite crucible, cooling rate 60-120°C/h to 500°.


Petrography of the bone-rock interface:



Tropper et al. (2006)

Olivine + Whitlockite + Anorthite + Spinel + Glass

Extremely well reproduced textures as well as mineral assemblages!



Tropper et al. (2006): Mineral chemistry of olivines



Olivine from the experiments.

Olivine from the slags.

 $2P+ (□)M_{1,2} \leftrightarrow 2Si + (Mg,Fe)M_{1,2}$

P-substitution in olivine could be reproduced but the extent is not the same!



Further bone-rock experiments were conducted at 1200°C using different rock types: orthogneiss, quartzphyllite amphibolite and paragneiss.





Paragneiss: overview

Spielmann (2013)



Part 4



Quartzphyllite: overview



- Assemblage at the bone-rock interface:
- Whitlockite + P-rich olivine + spinell + native Fe + glass
- High degree of melting throughout the sample!



Whitlockite: (Ca₉(Mg,Fe)[PO₃OH|(PO₄)₆])



Chemical composition of whitlockite **strongly depends on the nature** of the protolith rock composition.

Olivine

P-bearing olivines could also be reproduced. They show **up to** $4.5 \text{ wt.}\% P_2O_5$.

Clinopyroxene

P-bearing clinopyroxenes also formed. They show **up to 15 wt.** $\% P_2O_5!$



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Part 4 Conclusions

- Bone-rock experiments reproduce textures as well as mineralogy very well.
 - **P-bearing olivine and P-bearing clinopyroxene** formed in the experiments!
 - Whitlockite forms at the bone-rock interface!
 - No stanfieldite formed!



Discussion

The relevance of P-bearing phases in pyrometamorphic slags



How can we form whitlockite?

It is possible to balance mineral reactions in the **chemical system CaO-FeO-SiO₂-P₂O₅-** $Al_2O_3-H_2O$ between the phases **chamosite-quartz-fayalite-anorthite-whitlockite-H₂O**.

14 apatite + 7 chamosite + 7.5 quartz + 15.5 $O_2 \rightarrow 6$ whitlockite + 7 anorthite + 14.5 fayalite + 8 H₂O

Apatite + Chlorite + Quartz



Whitlockite + Plagioclase + Olivine



How can we form P-bearing olivines?

In the **chemical system CaO-FeO-SiO₂-P₂O₅-Al₂O₃-H₂O** mineral reactions between the phases **chamosite-quartz-fayalite-anorthite-hercynite-apatite-sarcopside-H₂O** can be calculated:

The **phopshate sarcopside** $Fe_3(PO_4)_2$ is structurally closely related to olivine (fayalite).

10 chamosite + 2 apatite + 10.5 quartz \rightarrow 3 sarcopside + 10 anorthite + 20.5 fayalite + 41 H₂O

20 chamosite + 2 apatite \rightarrow 3 sarcopside + 10 anorthite + 10 hercynite + 40.5 fayalit + 81H₂O

These reactions describe the formation of P-bearing olivine solid solutions very well!

Chlorite + Apatite ± Quartz = P-Olivine + Plagioclase + Spinel



Is bone apatite the only P-donor?NO!Wood contains up to $0.001 \text{ wt.\% P}_2O_5!$ Further P-donors are: food (meat) or fertlizier.....

Probe T005/013: Slag-tempered ceramics from the Kiechlberg. The mineral assemblage is olivine, clinopyroxene and glass. Glass (now altered) contains a lot of $P_2O_5!$



MgO	0.80
Al_2O_3	8.20
SiO ₂	7.39
P_2O_5	19.02
K ₂ O	0.14
CaO	3.13
TiO ₂	0.73
FeO	60.59
Total	100.00



How do P-rich silicates form?

P-rich olivine and P-rich clinopyroxene form by:

1.) Metastable growth: agrees with observed microdomains

2.) Extremely fast growth during cooling: no equilibrium!

3.) According to Boesenberg et al. (2010) mineral growth from a P-rich melt: in our samples rather mineral reactions instead of melt!

4.) Bone-rock experiments have shown that whitlockite and no stanfieldite forms!

5.) Whitlockite could indeed be a diagnostic phase!



Conclusions



Part 6: Conclusions

- Although **200 ritual immolation sites** occur throughout the Eastern Alps **only** 2 have been investigated from a mineralogical/petrological point of view.
- The investigated sites (Oetz, Goldbichl/Igls) are located on hill-tops and show abundant ceramic and bone fragments.
 - Slags occur (Oetz only little, Goldbichl, massive amounts)!
- Temperatures derived from the slags are >1000-1100°C under highly reducing (QFM) conditions.
- **Experimental investigations** verify these **temperatures** as well as the occurrence of **P-bearing olivine and whitlockte**.



 P-rich minerals which indicate the presence of a P-source in the fire are the following:

whitlockite, P-rich olivine, P-rich clinopyroxene, stanfieldite

 The following mineral assemblage has experimentally shown to be associated with bone-rock interactions is:

P-rich olivine ± P-rich clinopyroxene ONLY when coexisting with whitlockite!



Part 6: Conclusions

• P-rich olivine, P-rich clinopyroxene and stanfieldite form by decomposition of detrital apatite in the slags of the Goldbichl.

No bone material is involved in their formation!

• P-rich olivine and whitlockite have been found in the slags from Oetz.

Bone material might be involved in their formation!

 But bone apatite crystallinity of calcinated bones yields much lower temperatures: might be due to their position in "cooler" spots of the fire (e.g. at the surface).



Part 6: Conclusions

- The high temperatures deduced from the slags are compatible with core temperatures of large bone fires with a possible wind-driven air circulation.
- Archaeological implications for the Goldbichl site: the massive slags probably represent the last firing event of the immolation site: the ritual "closing" of the site by an enormous fire.
- Archaeological implications for the Oetz site: bone-rock interactions might have occurred. Only small amounts of slags have been found.
- The occurrence of the mineral whitlockite could be diagnostic for bone-rock interactions only if one considers archaeological, petrological and experimental data!



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