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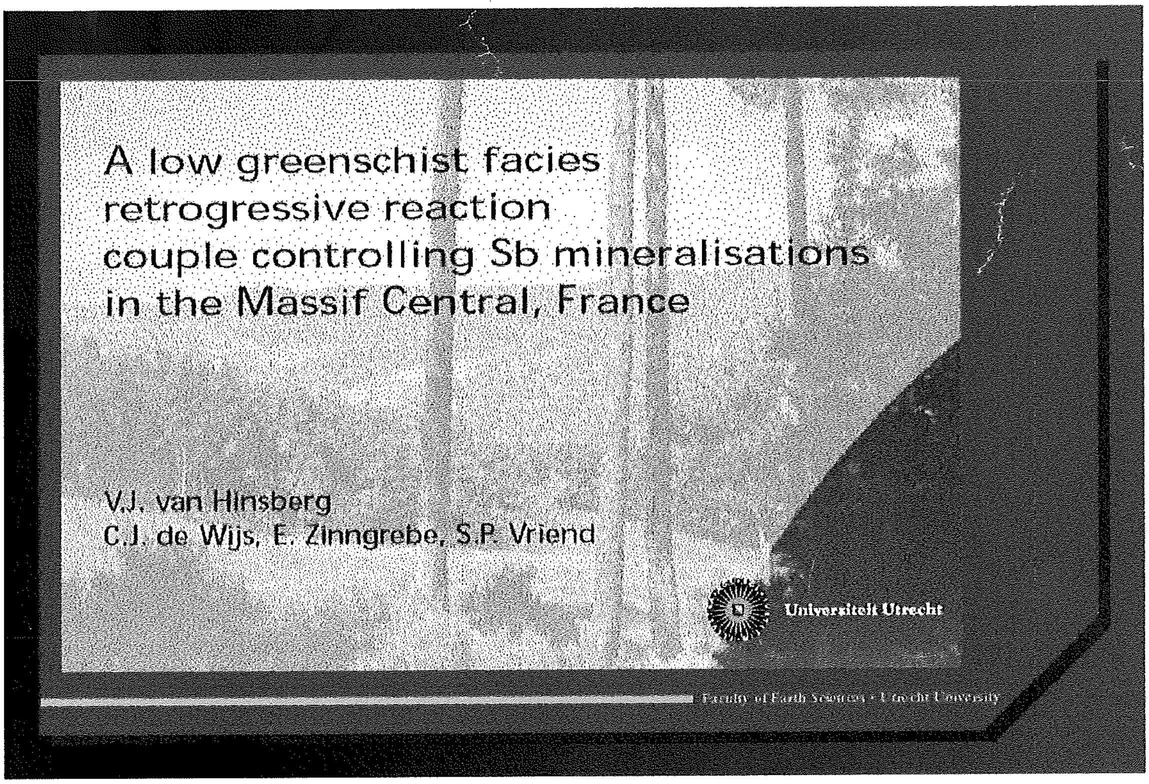

A low greenschist facies retrogressive reaction couple controlling Sb mineralisations in the Massif Central, France

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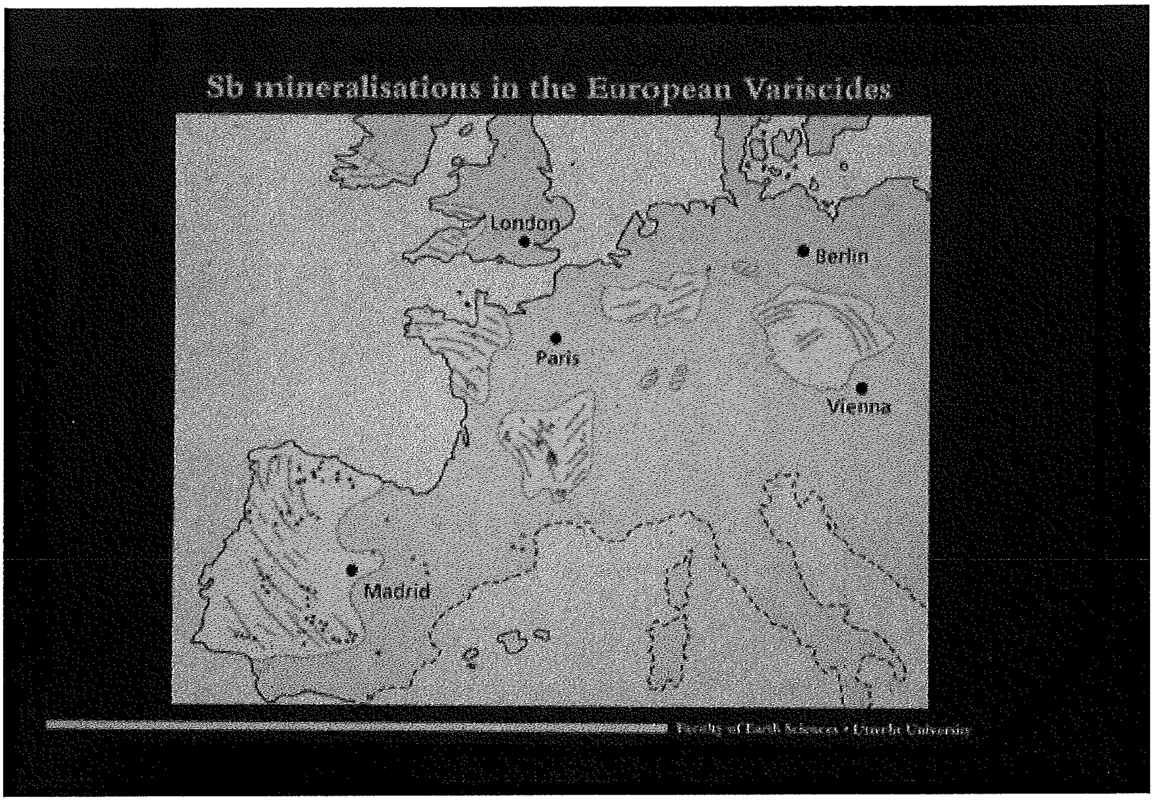
This presentation will present the preliminary results of the research, conducted by Hanno de Wijs and myself at the University of Utrecht in the Netherlands, on Sb deposits in the Massif Central in France.

The research consists of two parts. One concerning with the origin of the Sb and the mechanims of release and transport. The second theme is the deposition of Sb minerals at near surface conditions. This talk will focus on this second theme, presenting a new model for stibnite deposition in the French Massif Central.

Before going into the model I will give an overview of the regional geological setting of the area and the setting of the mineralisations.



Sb mineralisations in the European Variscides

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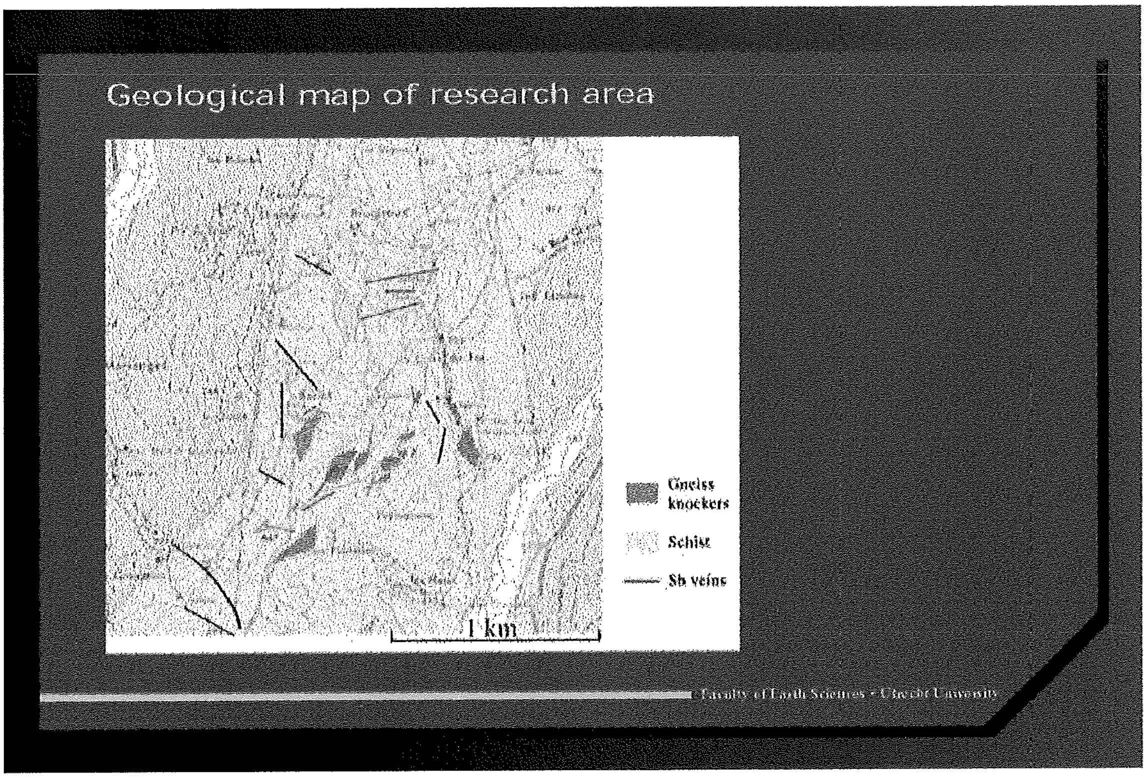
Sb depositions are present in a wide band in Europe, extending from the Massif Central to Normandy, bending over into Portugal and Spain. This band corresponds to the internal zone of the Variscides, which consists here of the suturezone between the Moldanubian microplate and Gondwana. Our research area is located in the square drawn on the map.



Geological map of research area

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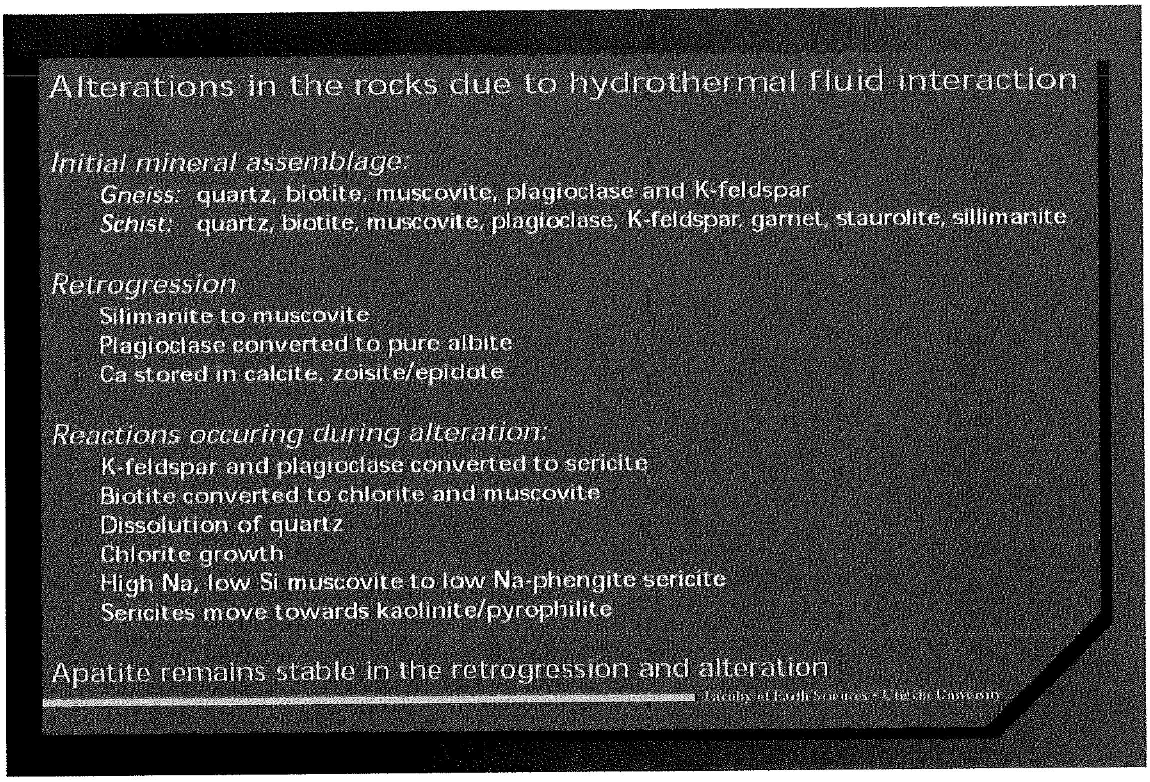
The research area is a hillcrest in between the Langeac graben and the valley of the Desges river. The geology of the area consists of a schist matrix folded around gneiss lenses which are up to 100 meters in size.

Veins cut through this assemblage, but these are only mineralised in the gneiss lenses.



Alterations in the rocks due to hydrothermal fluid interaction

Initial mineral assemblage:

Gneiss: quartz, biotite, muscovite, plagioclase and K-feldspar
Schist: quartz, biotite, muscovite, plagioclase, K-feldspar, garnet, staurolite, sillimanite

Retrogression

Silimanite to muscovite
Plagioclase converted to pure albite
Ca stored in calcite, zoisite/epidote

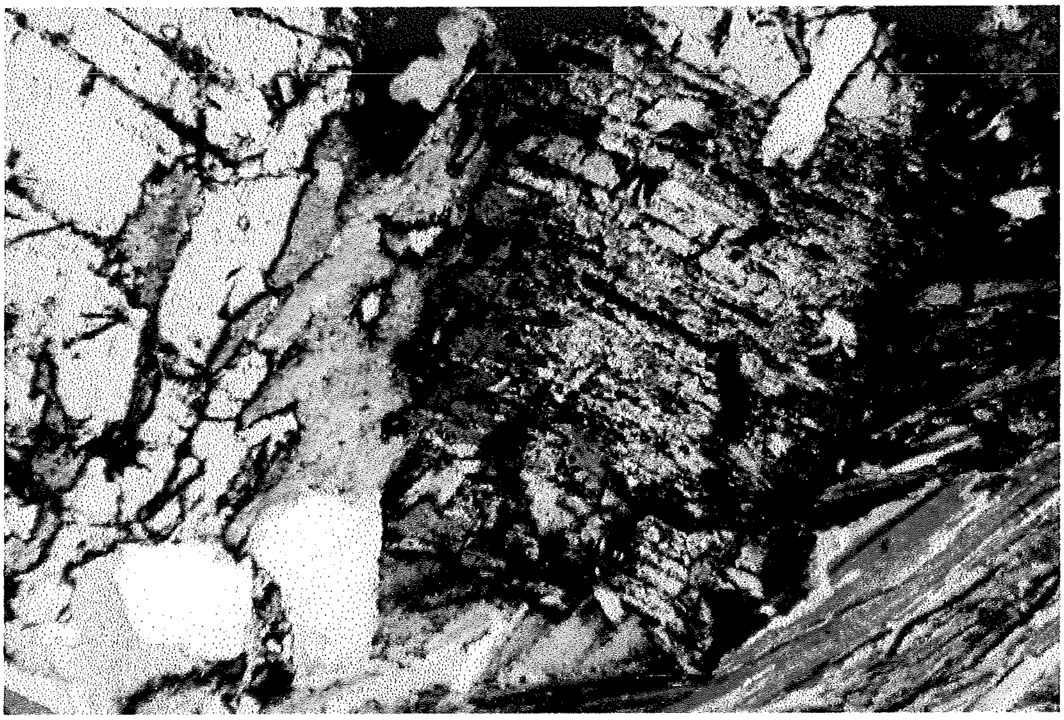
Reactions occuring during alteration:

K-feldspar and plagioclase converted to sericite
Biotite converted to chlorite and muscovite
Dissolution of quartz
Chlorite growth
High Na, low Si muscovite to low Na-phengite sericite
Sericites move towards kaolinite/pyrophilite

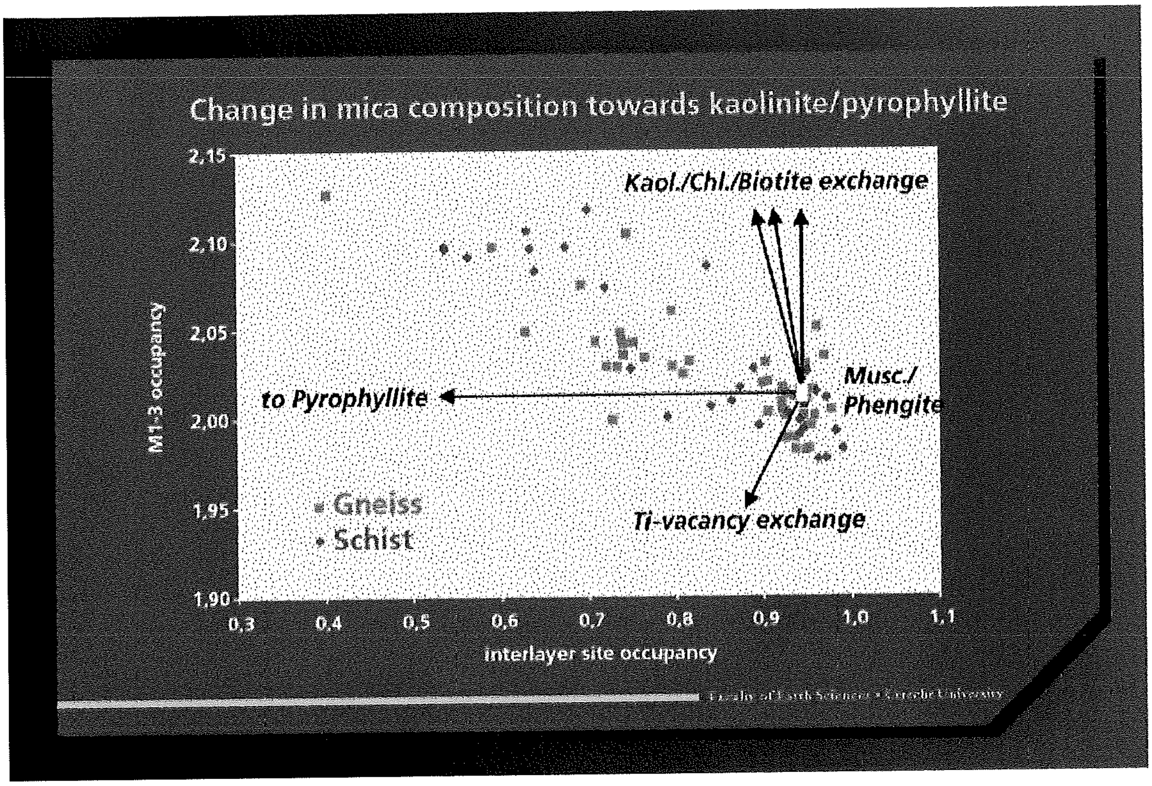
Apatite remains stable in the retrogression and alteration

The gneiss schist melange consists of typical gneisses embedded in garnet staurolite schist, which have been metamorphosed to amphibolite facies.

During uplift the gneiss-schist assemblage has been retrograded. The most important change during retrogression is the conversion of plagioclase to the albite endmember. The Ca is stored in zoisite/epidote minerals and calcite.



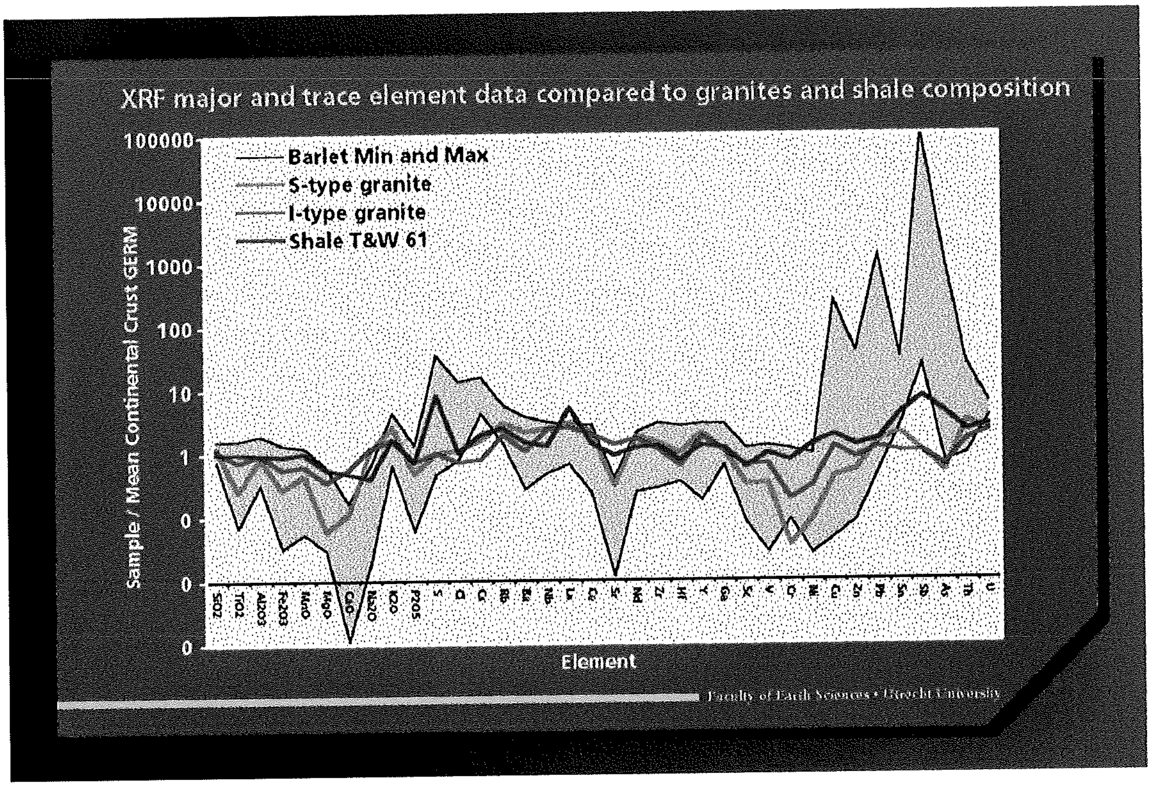
The retrogression is followed by an episode of hydrothermal alteration. This results in strong sericitisation of the rocks, most importantly conversion of the feldspars into sericite



Change in mica composition towards kaolinite/pyrophyllite

During the alteration the composition of the newgrown muscovites changes from the metamorphic near stoichimetric muscovite composition towards kaolinite and pyrophyllite, as can be seen in this plot of interlayer site occupancy on the lower axis and M1-3 occupancy on the vertical axis.

This trend is present in the different generations of muscovite in the schists as well as in the gneisses.



XRF major and trace element data compared to granites and shale composition

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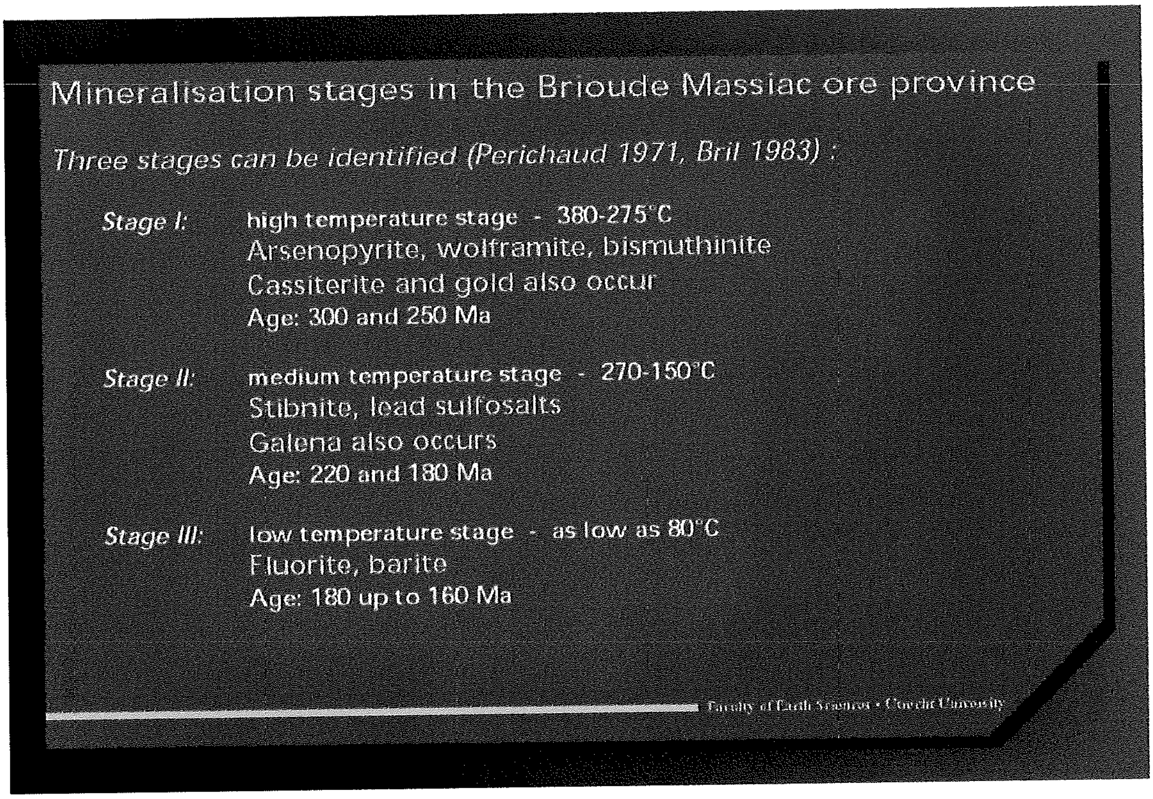
It is interesting to note that the alteration is not only present around the veins, but can be recognised in the complete area. This is shown in a diagram of the whole rock chemistry.

This diagram shows the composition of the rocks relative to average continental crust. On the bottem axis are shown the major elements followed by the minor elements. It is clear from this diagram that there is a strong Ca + Sr anomaly. These elements have been leached from the gneisses as well as the schists.

Cl and Cs, which are volatile elements, are clearly enriched in the schists and gneisses as are the ore elements Pb, Cu, Zn and Sb.

The alteration has thus affected the whole area.

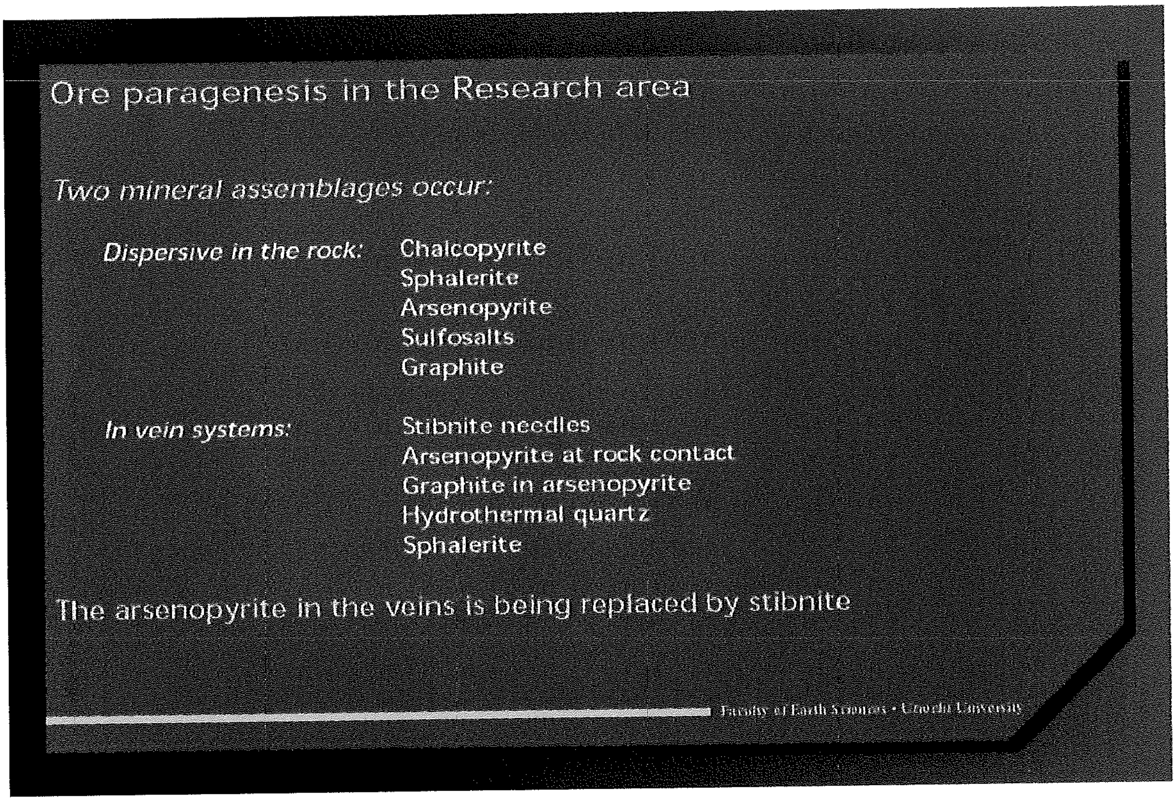


Mineralisation stages in the Brioude Massiac ore province

Three stages can be identified (Perichaud 1971, Bril 1983) :

Stage I:	high temperature stage - 380-275°C Arsenopyrite, wolframite, bismuthinite Cassiterite and gold also occur Age: 300 and 250 Ma
Stage II:	medium temperature stage - 270-150°C Stibnite, lead sulfosalts Galena also occurs Age: 220 and 180 Ma
Stage III:	low temperature stage - as low as 80°C Fluorite, barite Age: 180 up to 160 Ma

Our research area is part of the larger Brioude-Massiac ore province. This province has been affected by three consecutive ore forming stages, from a high temperature stage to a low temperature stage. Our stibnite deposits are part of the second stage, which is a medium temperature stage with temperatures between 250 and 150 oC. The age of these deposits is about 200 Ma and they are characterised by stibnite.



Ore paragenesis in the Research area

Two mineral assemblages occur:

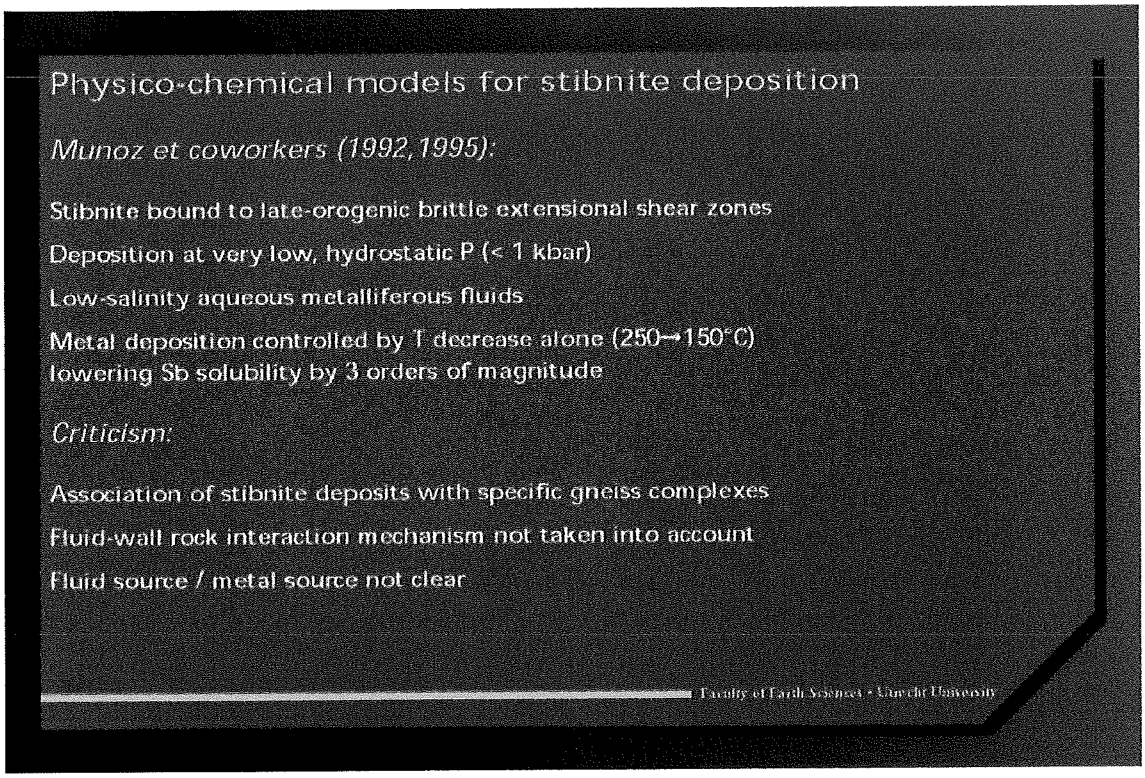
Dispersive in the rock:
- Chalcopyrite
- Sphalerite
- Arsenopyrite
- Sulfosalts
- Graphite

In vein systems:
- Stibnite needles
- Arsenopyrite at rock contact
- Graphite in arsenopyrite
- Hydrothermal quartz
- Sphalerite

The arsenopyrite in the veins is being replaced by stibnite

Two ore paragenesis are present in the rocks in the research area. Chalcopyrite, sphalerite, arsenopyrite and graphite are found dispersive in the rock.

The stibnite is found selectively in veins, together with sphalerite and hydrothermal quartz.



Physico-chemical models for stibnite deposition

Munoz et coworkers (1992,1995):

Stibnite bound to late-orogenic brittle extensional shear zones

Deposition at very low, hydrostatic P (< 1 kbar)

Low-salinity aqueous metalliferous fluids

Metal deposition controlled by T decrease alone (250→150°C)
lowering Sb solubility by 3 orders of magnitude

Criticism:

Association of stibnite deposits with specific gneiss complexes

Fluid-wall rock interaction mechanism not taken into account

Fluid source / metal source not clear

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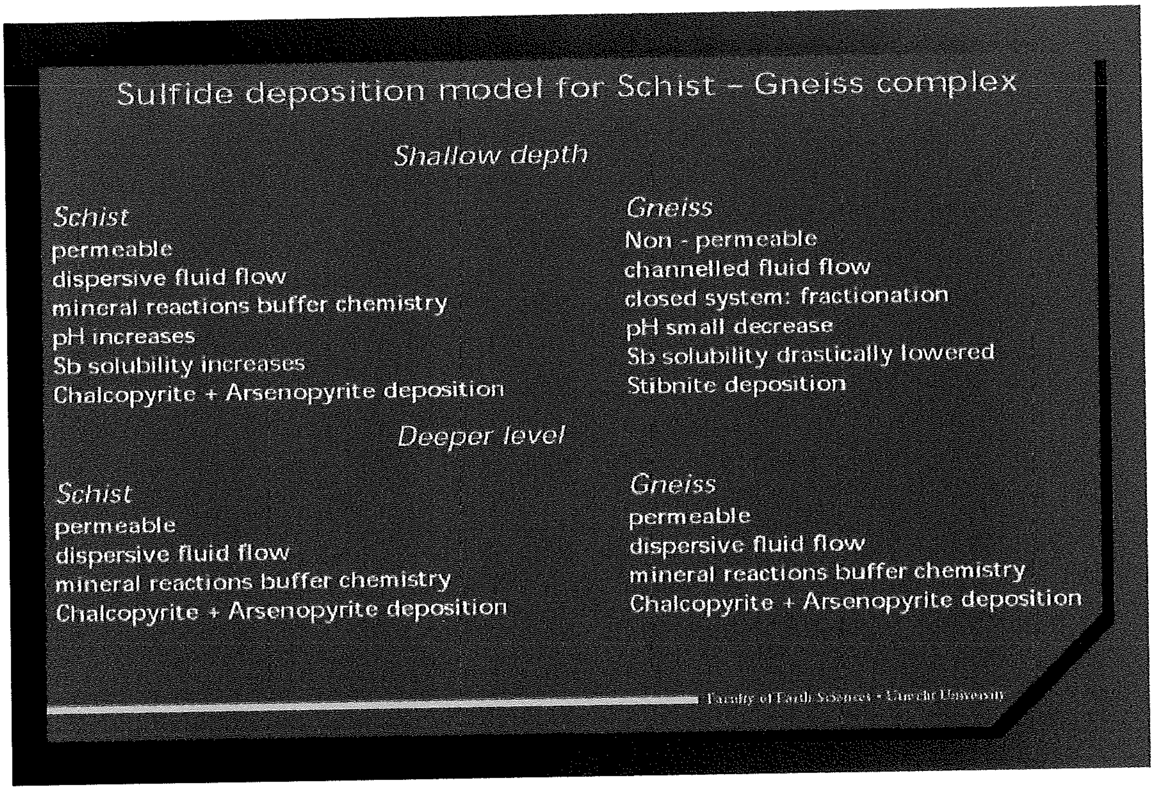
Plenty of literature is available on these deposits, including publications on stibnite deposition models. The most extensive description of the mechanisms of stibnite deposition has been presented by Munoz and coworkers.

In their model the stibnite deposits are related to brittle extensional settings, where the stibnite precipitates from low salinity fluids by temperature decrease alone.

This model however fails to explain why the stibnite only occurs in the gneiss lenses, while the alteration has affected the whole assemblage. Furthermore the source of the antimony has not been explained.



Sulfide deposition model for Schist – Gneiss complex

Shallow depth

Schist	*Gneiss*
permeable	Non - permeable
dispersive fluid flow	channelled fluid flow
mineral reactions buffer chemistry	closed system: fractionation
pH increases	pH small decrease
Sb solubility increases	Sb solubility drastically lowered
Chalcopyrite + Arsenopyrite deposition	Stibnite deposition

Deeper level

Schist	*Gneiss*
permeable	permeable
dispersive fluid flow	dispersive fluid flow
mineral reactions buffer chemistry	mineral reactions buffer chemistry
Chalcopyrite + Arsenopyrite deposition	Chalcopyrite + Arsenopyrite deposition

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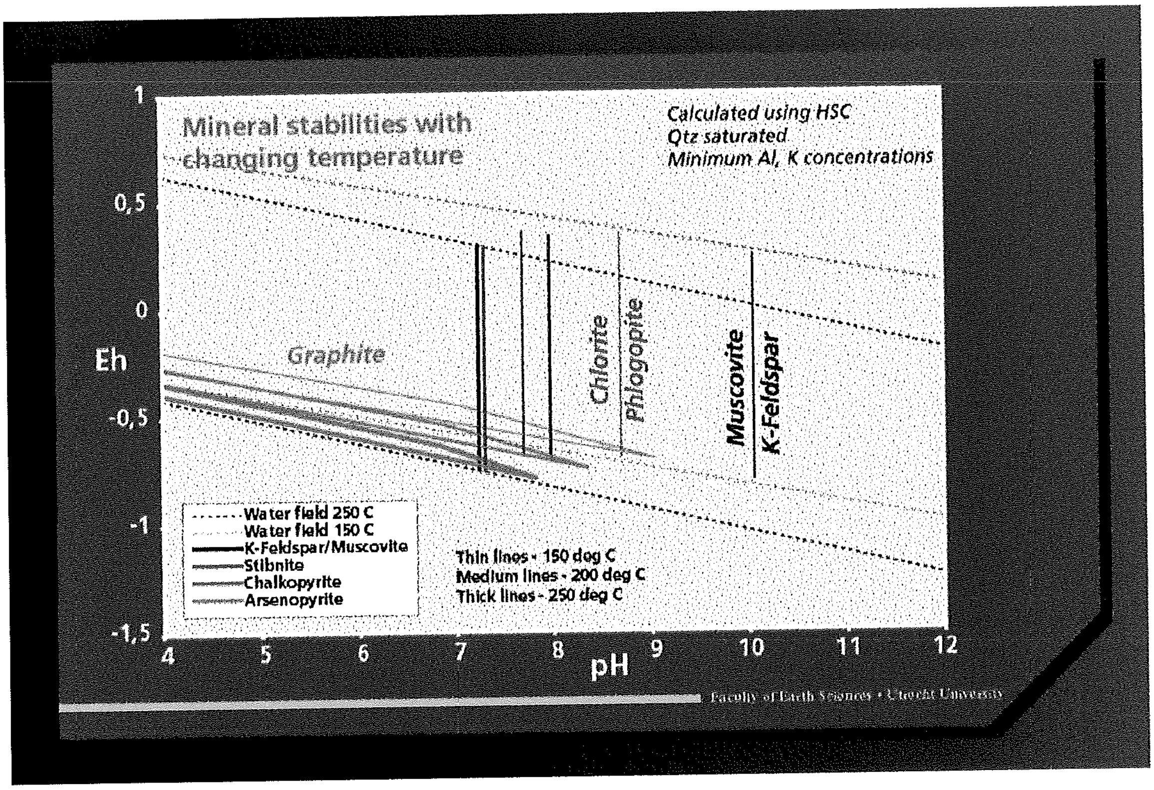
Therefore we have focussed for our model on this specific preference for the gneiss lenses. There has to be some difference in the chemical conditions between the different rock types to explain the observed preference.

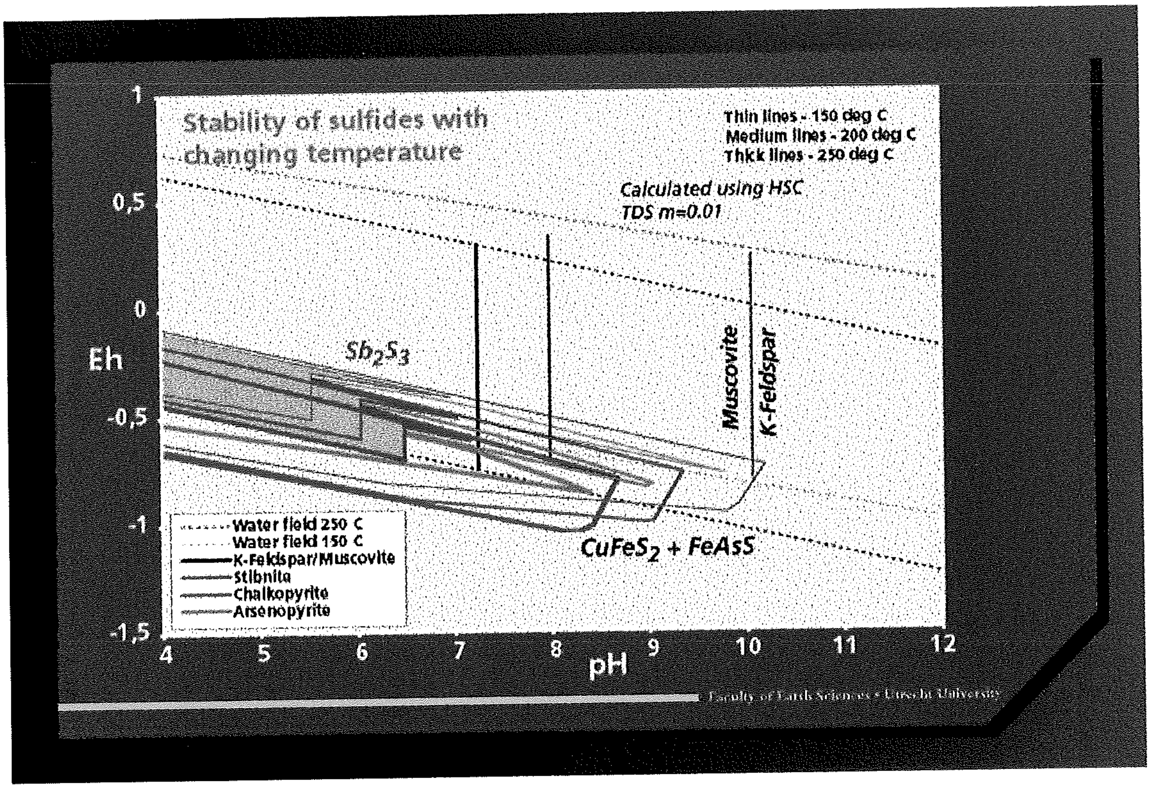
These conditions are buffered in the rock by mineral reactions that are occuring. We have therefore conducted thermodynamic modelling on the assemblage that is present in our rocks.



This diagram is an Eh-pH diagram showing the mineral reactions that we have observed in the rocks and the changes in the position of these with changing temperature. The graphite fuield has also been included for the different temperatures. The thick lines are for the highest temperature, with thinner lines for lower tempertures.

At the highest temperature, the Eh-pH conditions are nicely defined and the different reactions agree very well with each other. With decreasing temperature the fluid is pulled towards higher pH.

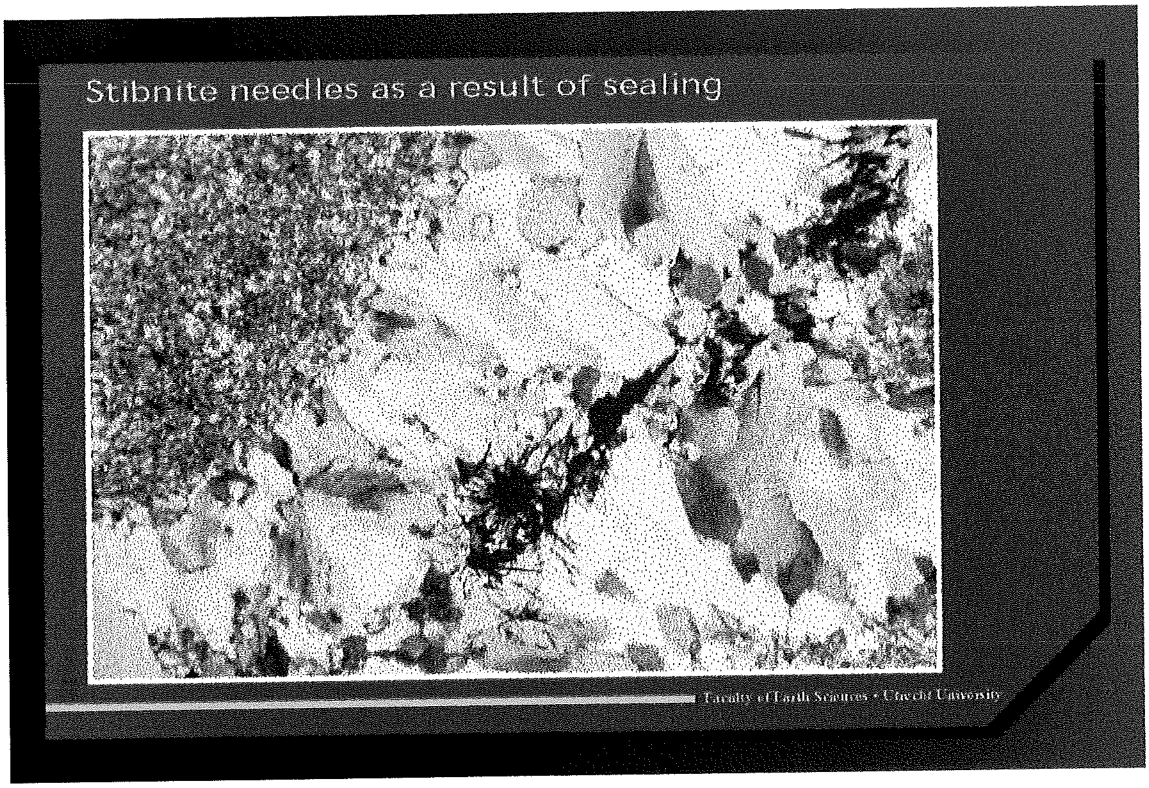
if we now look what the effect is on the sulfide stability:



This diagram shows an Eh-pH diagram of the stability fields of chalcopyrite, arsenopyrite and stibnite for different temperatures. The temperatures again decrease from thick to thin lines. The K-feldspar to muscovite reaction has been included to show the conditions defined by this buffer.

It is clear from this diagram that chalcopyrite and arsenopyrite will precipitate with the conditions present in the rocks. Three will however not be any stibnite deposition. With temperature decrease we actually pull away from the stibnite field.

So how DO we form stibnite deposits then?



Stibnite needles as a result of sealing

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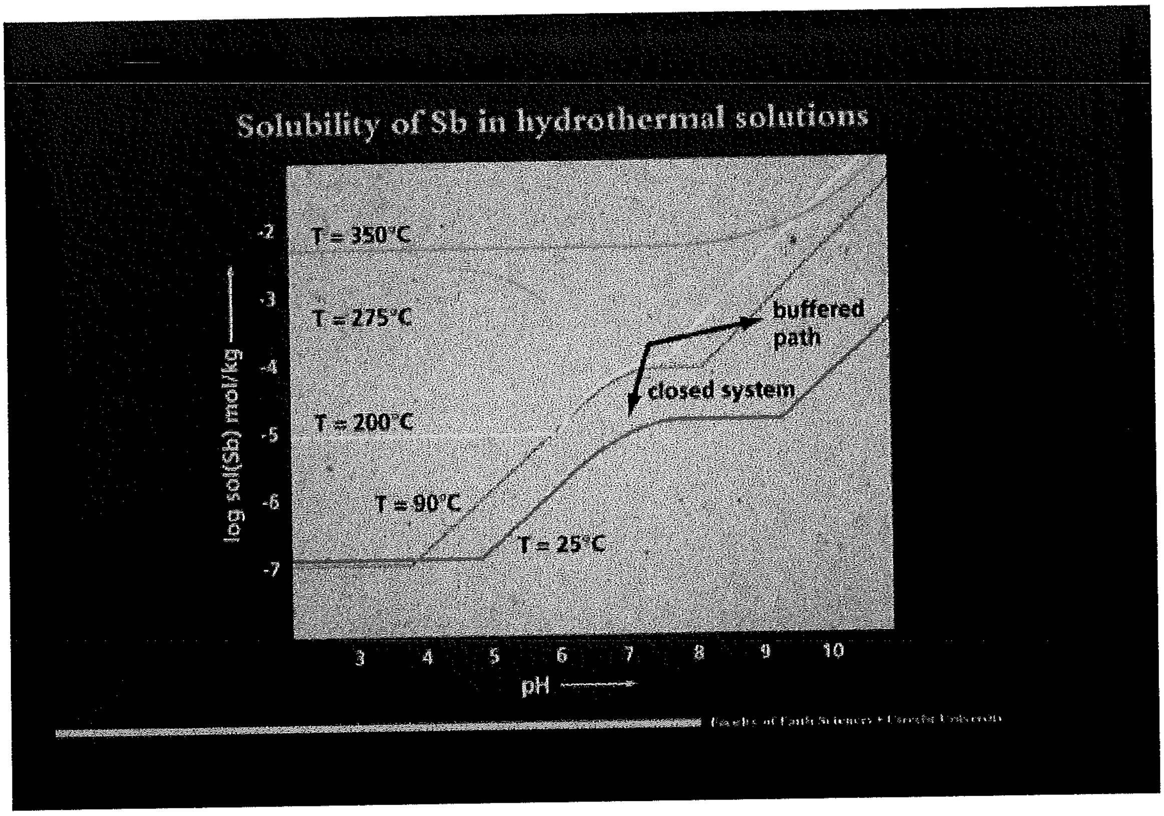
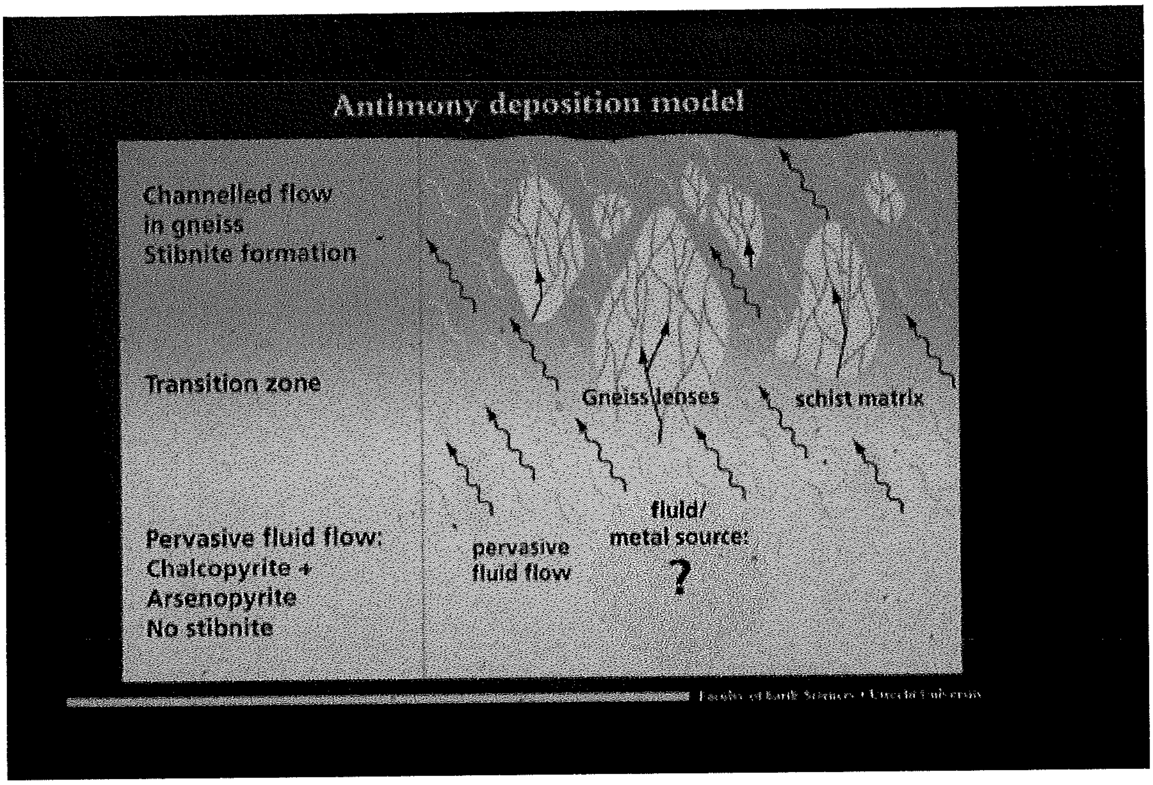
To answer this question we have gone back to the rocks. If you look at how the stibnite is present in the rock then it is only present in veins in the gneiss lenses that are sealed by quartz from the country rock and therefore sealed from the buffering reactions in this country rock.



Solubility of Sb in hydrothermal solutions

When the hydrothermal fluid is decoupled from the buffering reactions in the rock over a temperature gradient, it will follow a path as shown in the diagram by the line marked as "closed system" This will result in a strong decrease in the solubility of Sb and ultimately lead to stibnite precipitation. While in the schists, which remain permeable to fluid flow, the fluid is buffered and no stibnite will precipitate.



Antimony deposition model

Channelled flow
in gneiss
Stibnite formation

Transition zone

Pervasive fluid flow:
Chalcopyrite +
Arsenopyrite
No stibnite

This results in a model where there is pervassive fluid flow at depth through the gneisses and the schists with chalcopyrite and arsenopyrite deposition. This results in relative enrichment of the fluid in Sb.

At a higher level the gneisses become impermeable and the fluid flow is concentrated in veins that are sealed from the buffering reactions in the country rock. A temperature gradient on these fluids results in a strong decrease in the solubility of Sb and consequent deposition of stibnite. In the schists the permeability remains and stibnite deposition is inhibited by the mineral reactions that pull the conditions in the rock away from the stibnite field.

The big question is still what the source of the Sb is. We have not yet looked into this in detail but the age of Pb in the deposits nicely coincides with peak metamorphism of granulites in the lower crust. We therefore tentatively identify the dehydration of the granulites as the source of the Sb.