Fluorine and Chlorine in Alkaline Rocks and A-type Granites

Using the fluorine and chlorine content of Amphibole, Apatite and Biotite to monitor magma halogen content

Chilwa Province, Malawi, and Carboniferous A-type granites from western Argentina

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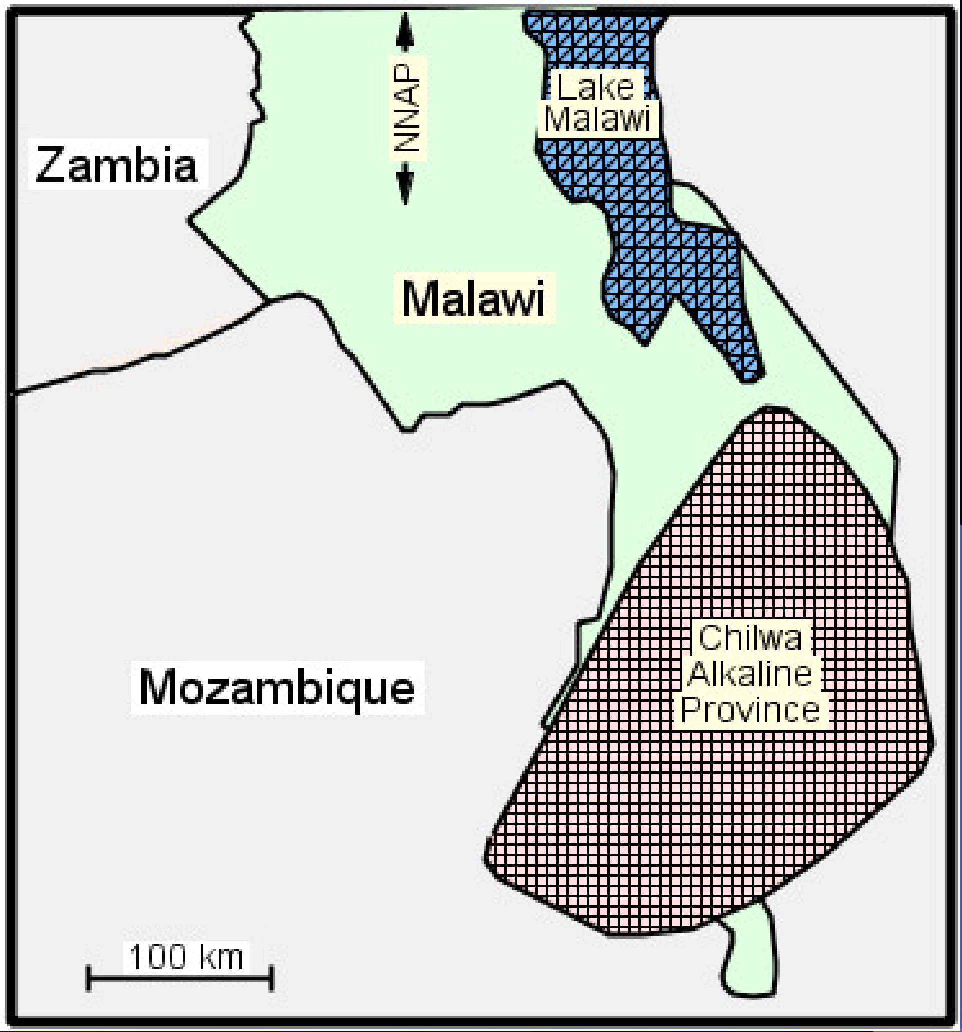
Fluorine and Chlorine in felsic magmas

- There are three common minerals that contain F and Cl – amphibole, apatite, and mica.
- Titanite, a mineral that is common in some A-type granites and alkaline rocks, also contains significant amounts of F.
- Models exist for calculating the F and Cl content of melts using apatite and biotite chemistry.
- No model currently exists for calculating the F and Cl content of a melt using amphibole chemistry.
- Variations in the F and Cl content in the various halogen containing minerals can be used to monitor changes in magma F and Cl content. Given that these minerals will form at different times during the crystallization of a magma they can provide a picture of the variation in F and Cl content of the magma with crystallization.
- Electron microprobe analysis of these minerals for F and Cl is far from trivial. I will be happy to discuss our approach after the talk.

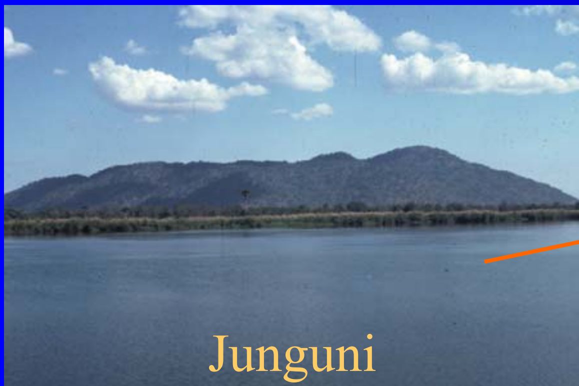
Chilwa alkaline province – Location

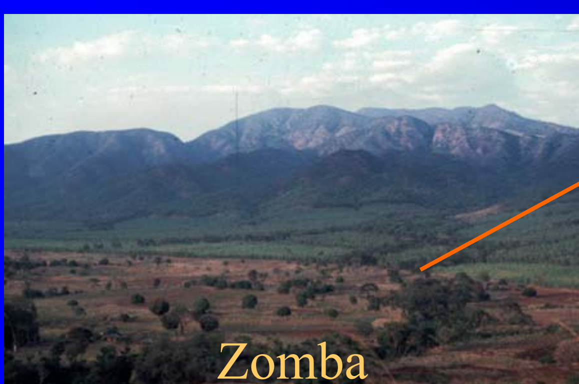
The Cretaceous age Chilwa Alkaline Province (CAP) is located in southern Malawi near the southern end of the present-day East African Rift System.

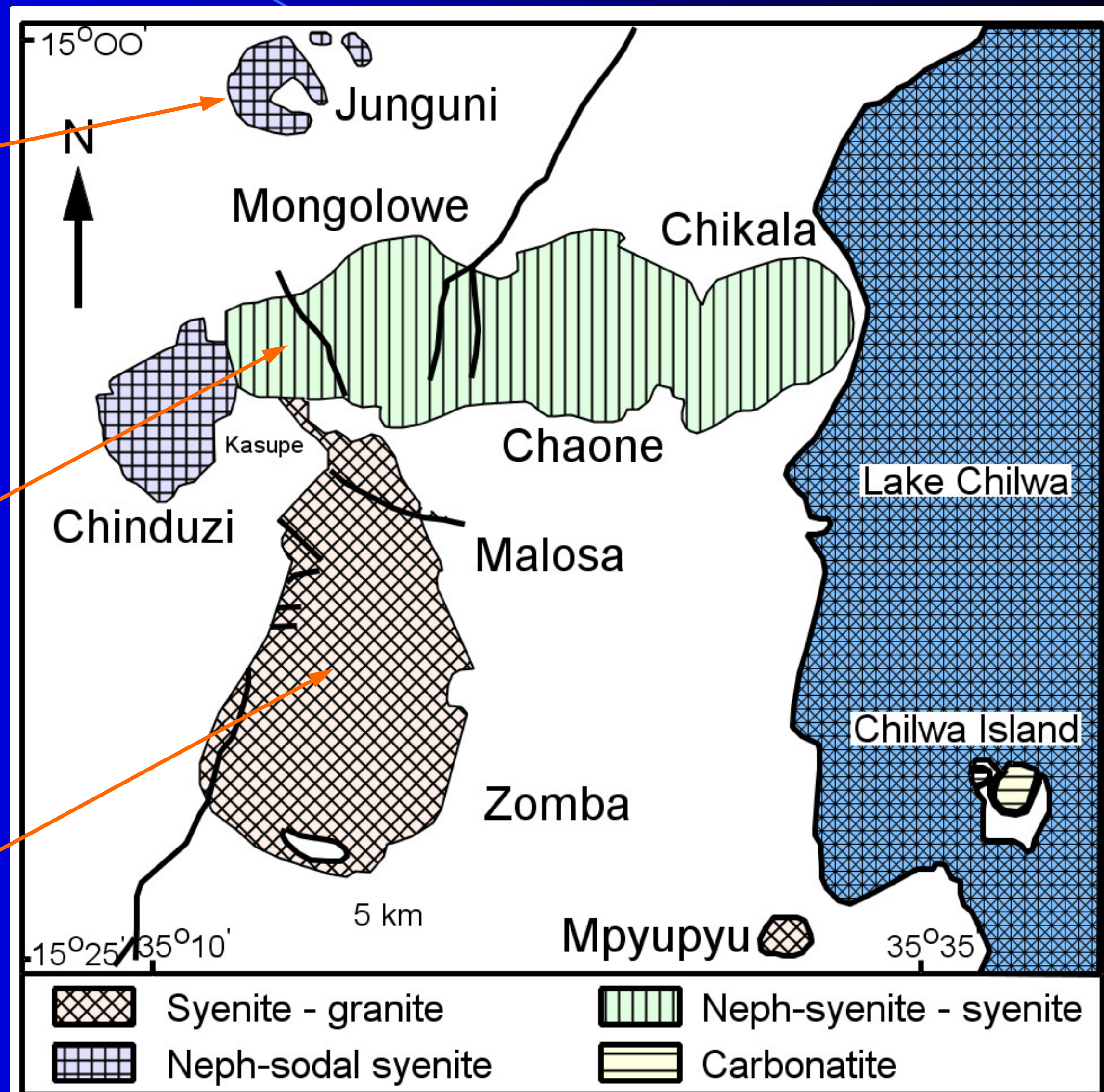


Geology of the Chilwa Alkaline Province

Lithologies: carbonatite, nepheline-sodalite syenite, nepheline syenite, syenite, granite







Major lithologies of the Chilwa Province

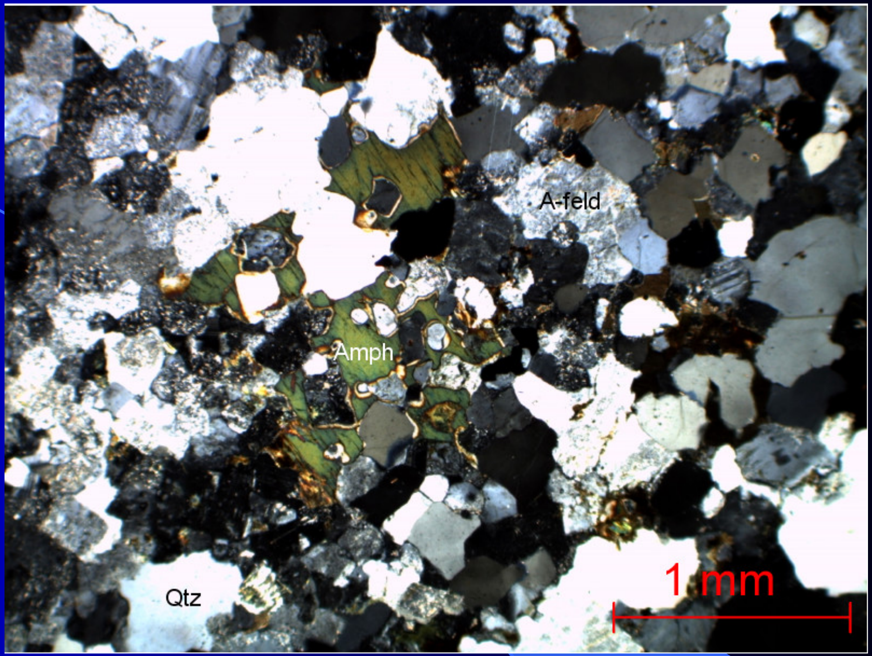
- Metavolcanics (basanites) and olivine nephelinites
- Nepheline-sodalite syenites and nepheline syenites
- Syenites and alkali granites

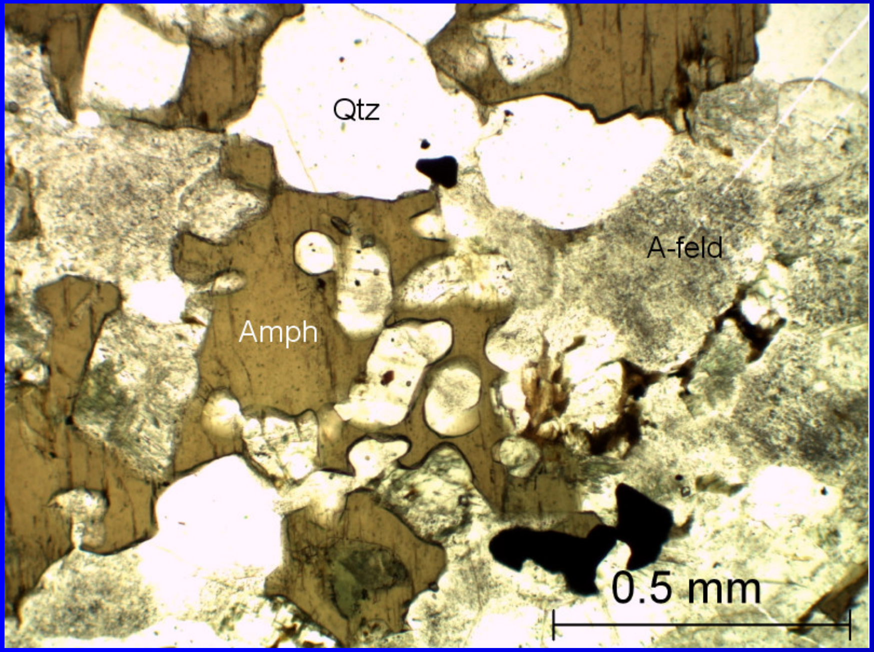
Sequence of emplacement

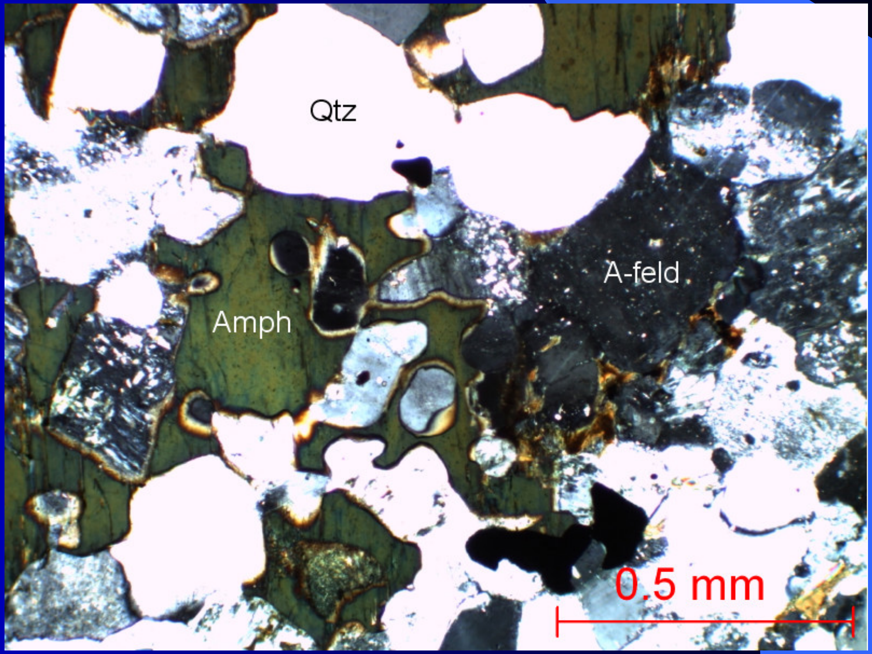
- Lava flows (basanites) and nepheline-sodalite syenites
- Nepheline syenites and syenites
- Syenites and alkali granites

The pattern is increasing silica content with decreasing age

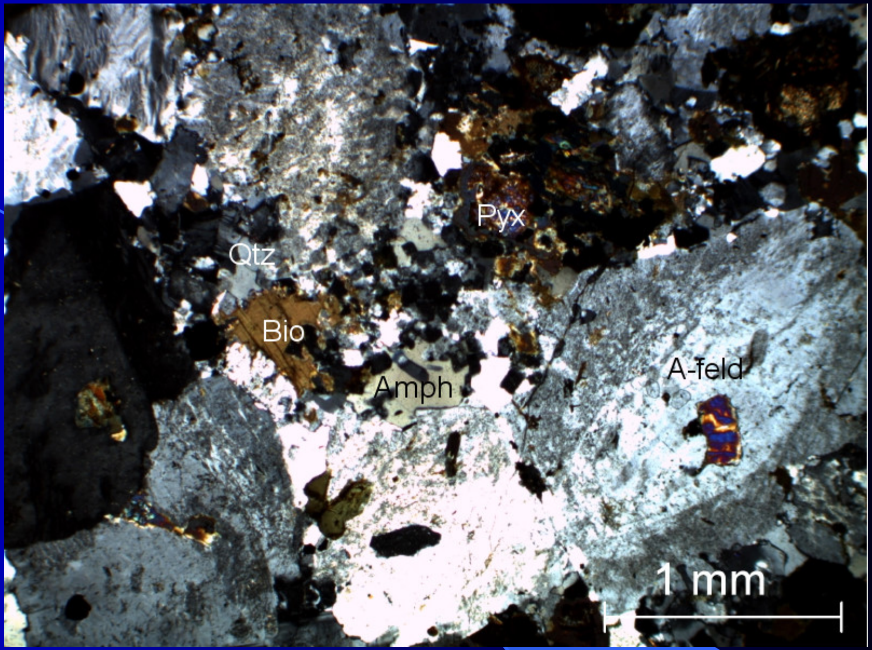
P19(4) – Medium grained fayalite-biotite-amphibole granite. Zomba.

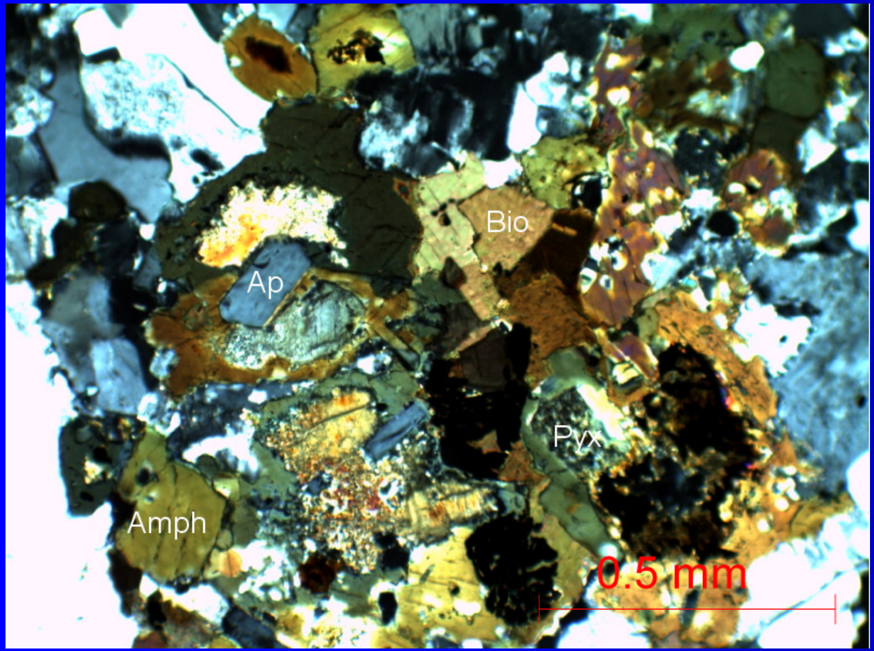


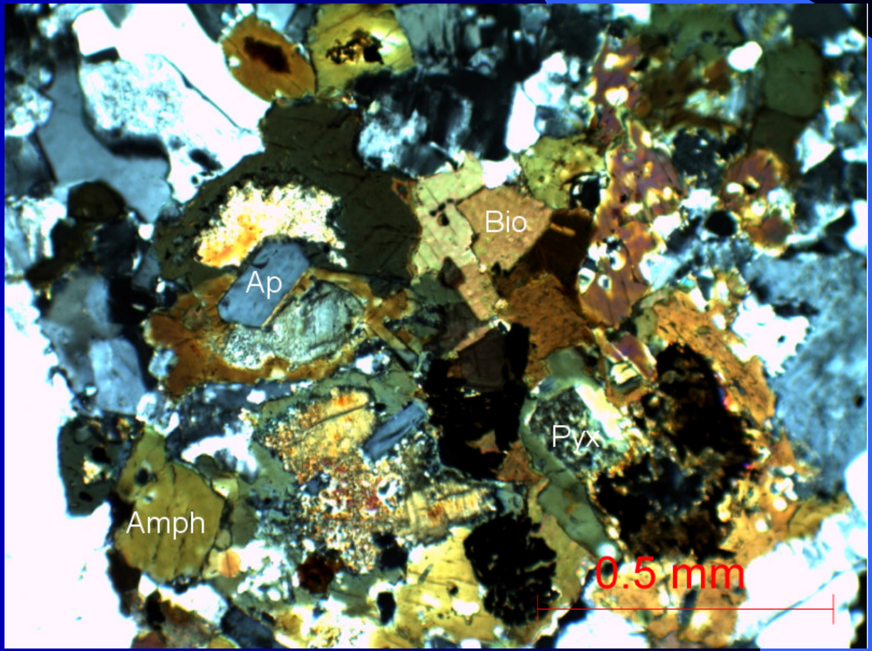




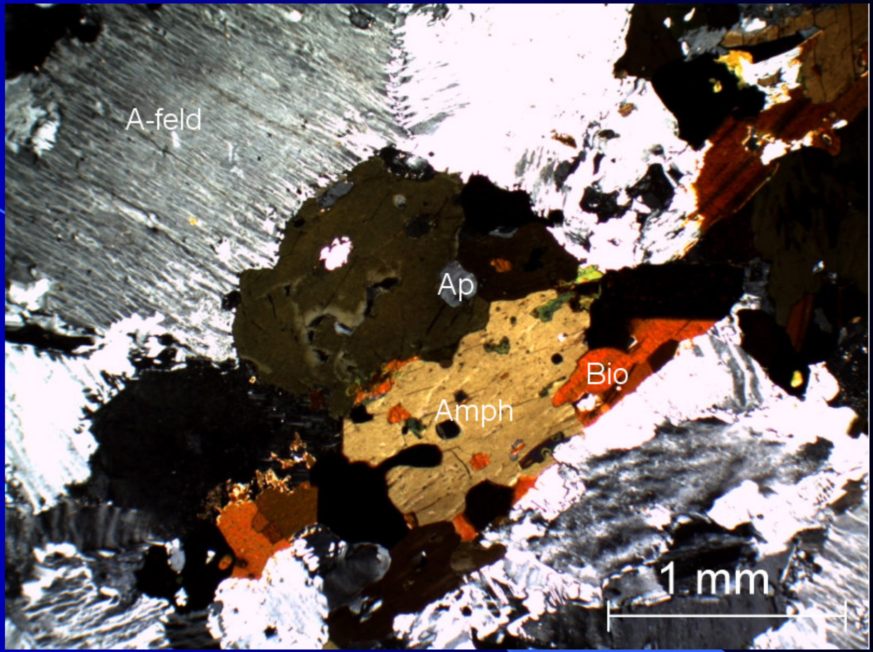
P19(1) – Porphyritic pyxoxene-amphibole-biotite-quartz syenite. Zomba.

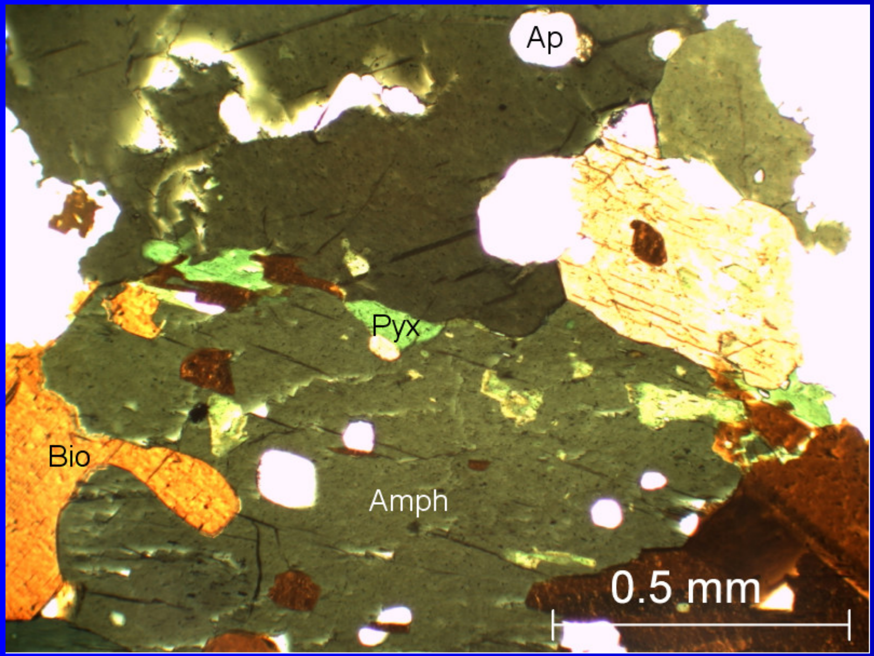


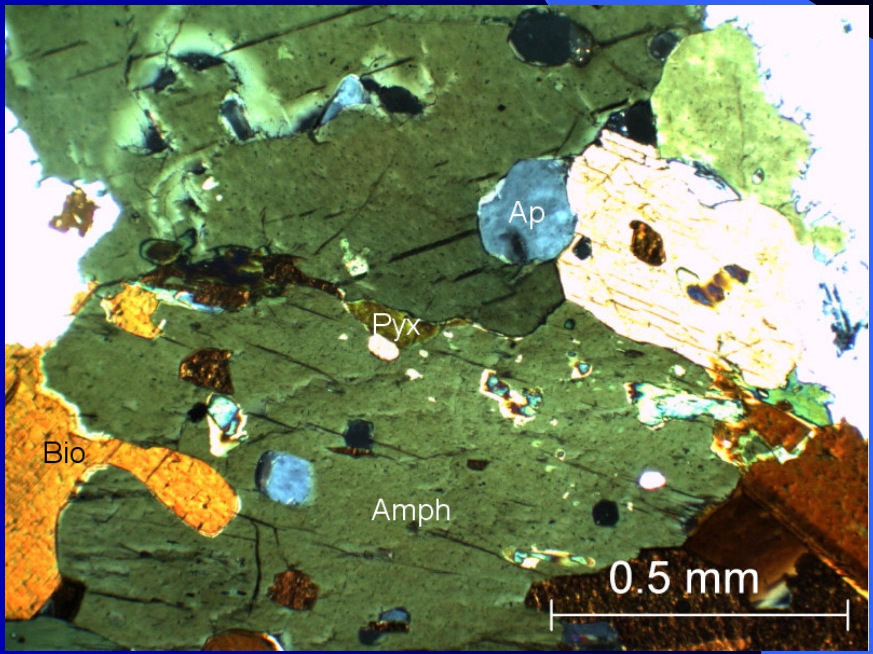




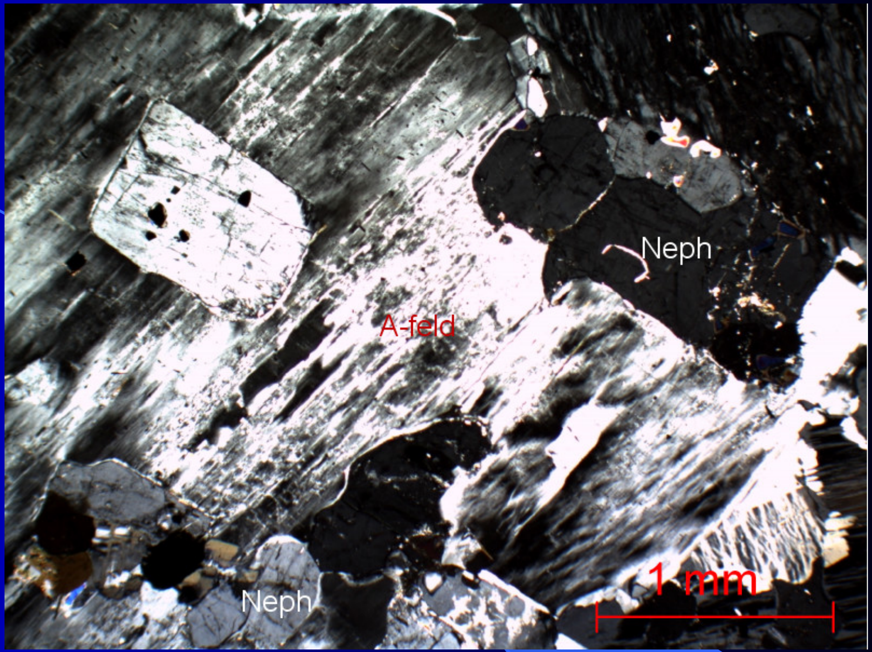
P20(4) – Medium grained amphibole-biotite-aegirine-nepheline syenite. Chinduzi.

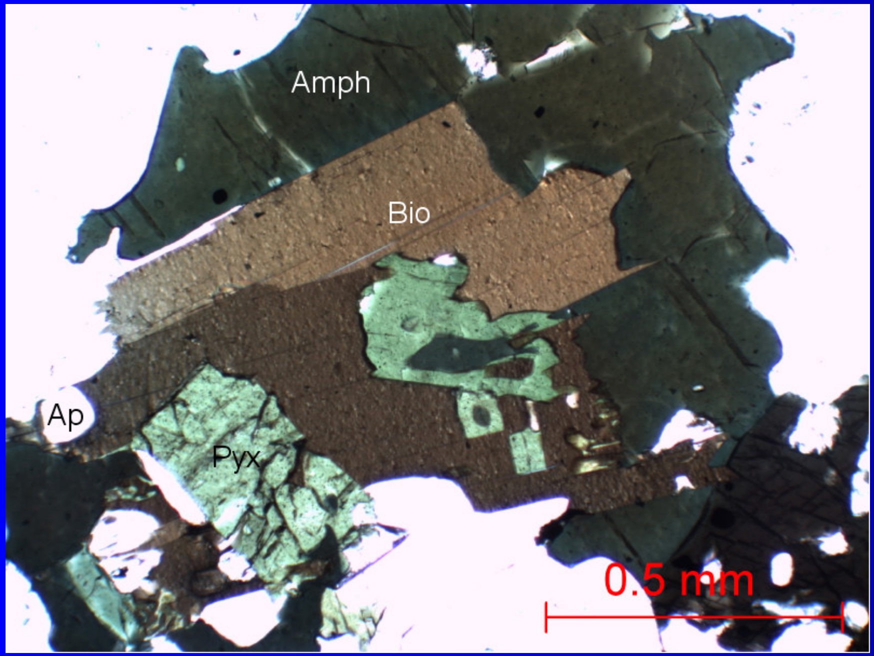


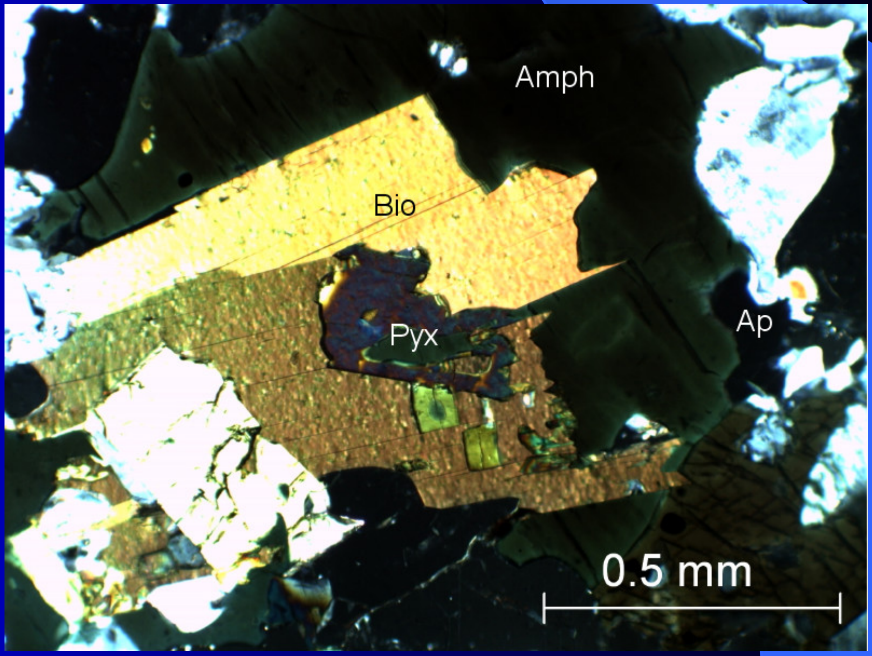




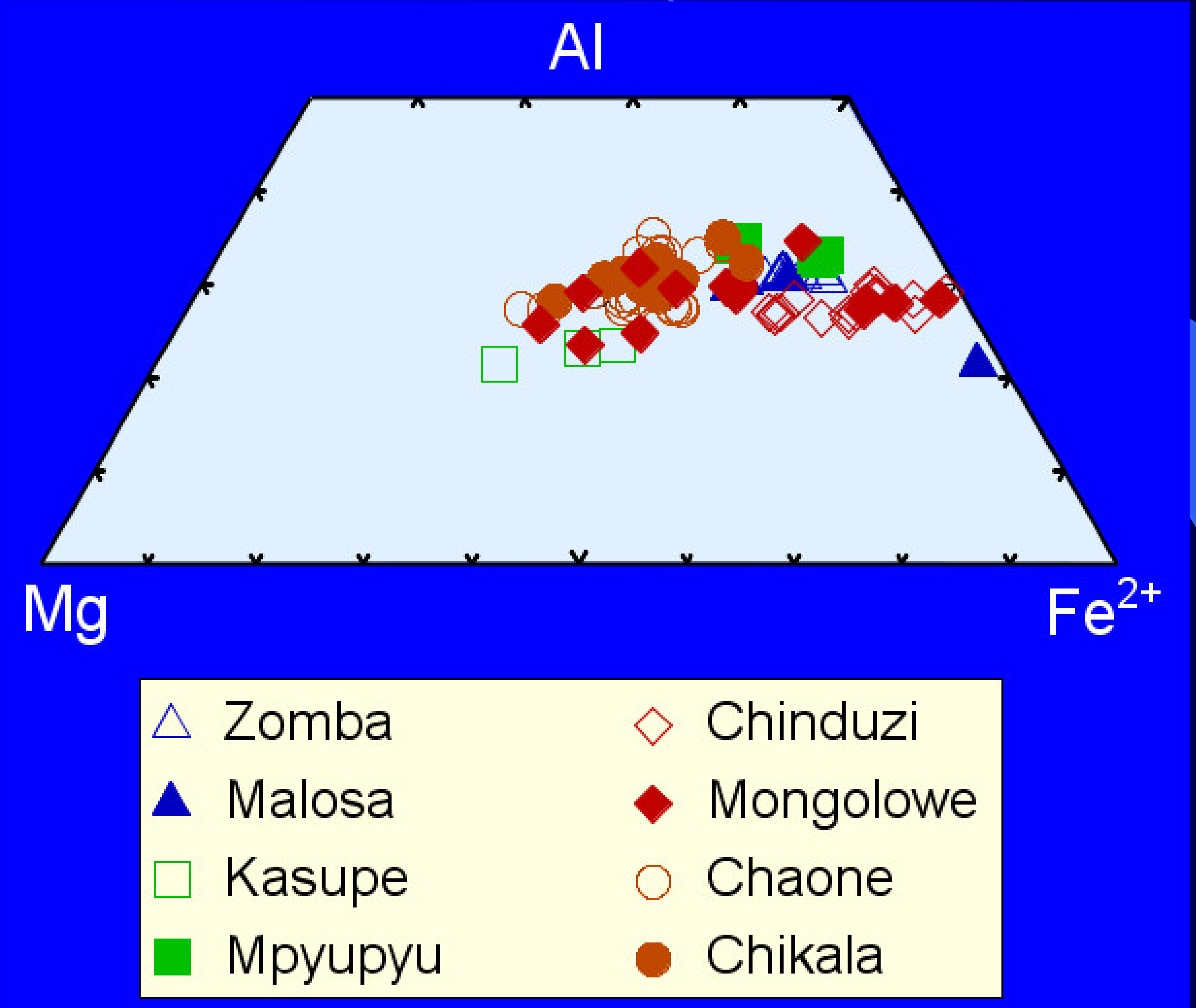
P21(17) – Medium- to coarse-grained amphibole-biotite-aegirine-nepheline-sodalite syenite. Chaone.



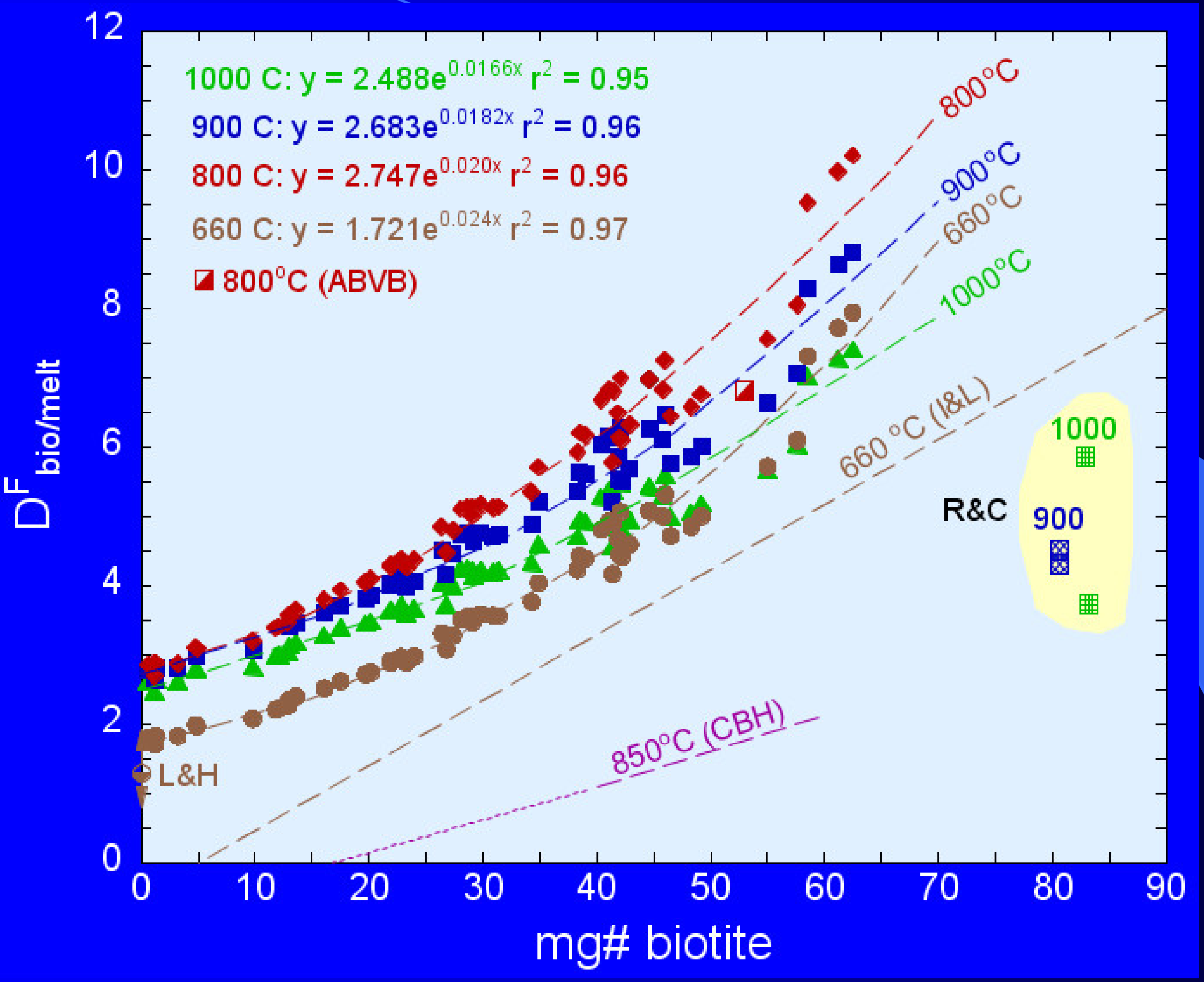




Chemical composition of Chilwa biotites



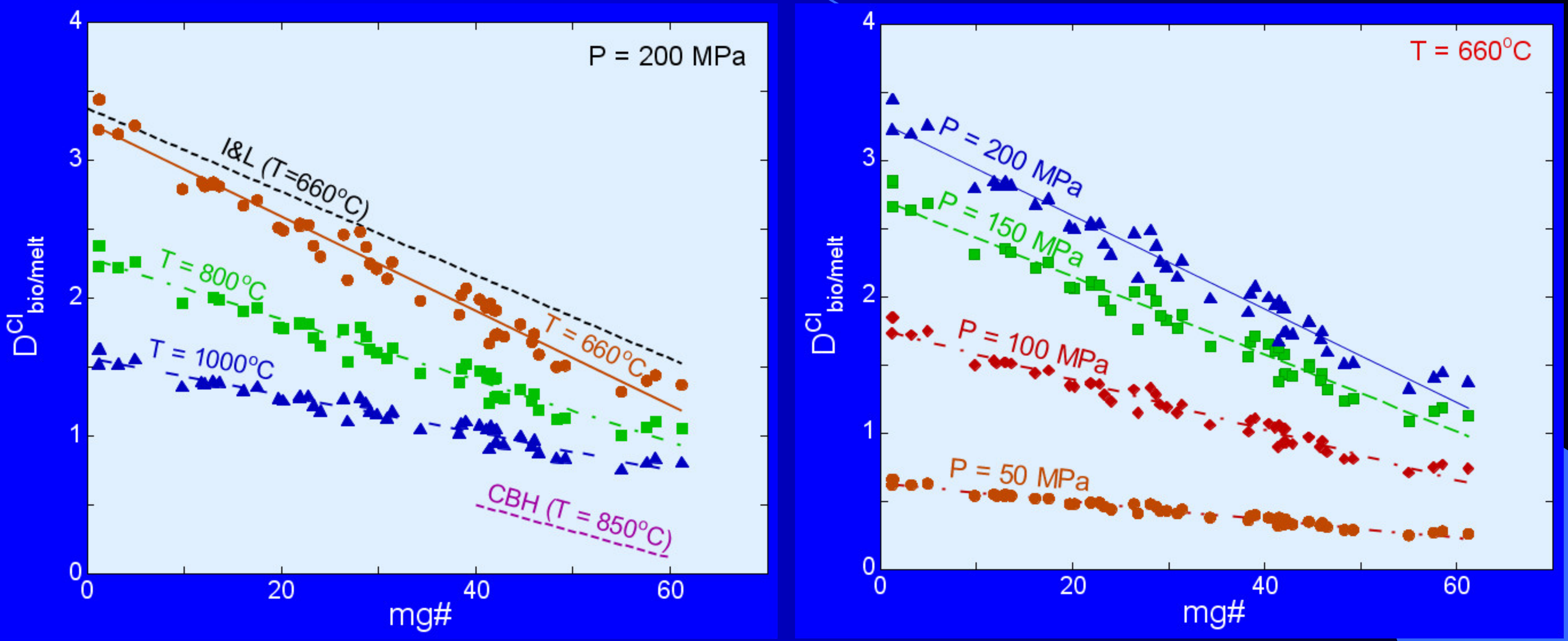
Partitioning of F Between Biotite and Melt as a Function of Temperature



$\text{Log}(f_{H2O}/f_{HF}) = [1000/T]*[2.37 + 1.1X_{Mg} + 0.43 - \log(X_F/X_{OH})]$ (Munoz, 1992)

$D_F^{aq/melt} = -0.56 + .00093T$ (°C) [Piccoli and Candela, 1994]

Partitioning of Cl Between Biotite and Melt as a Function of Temperature and Pressure

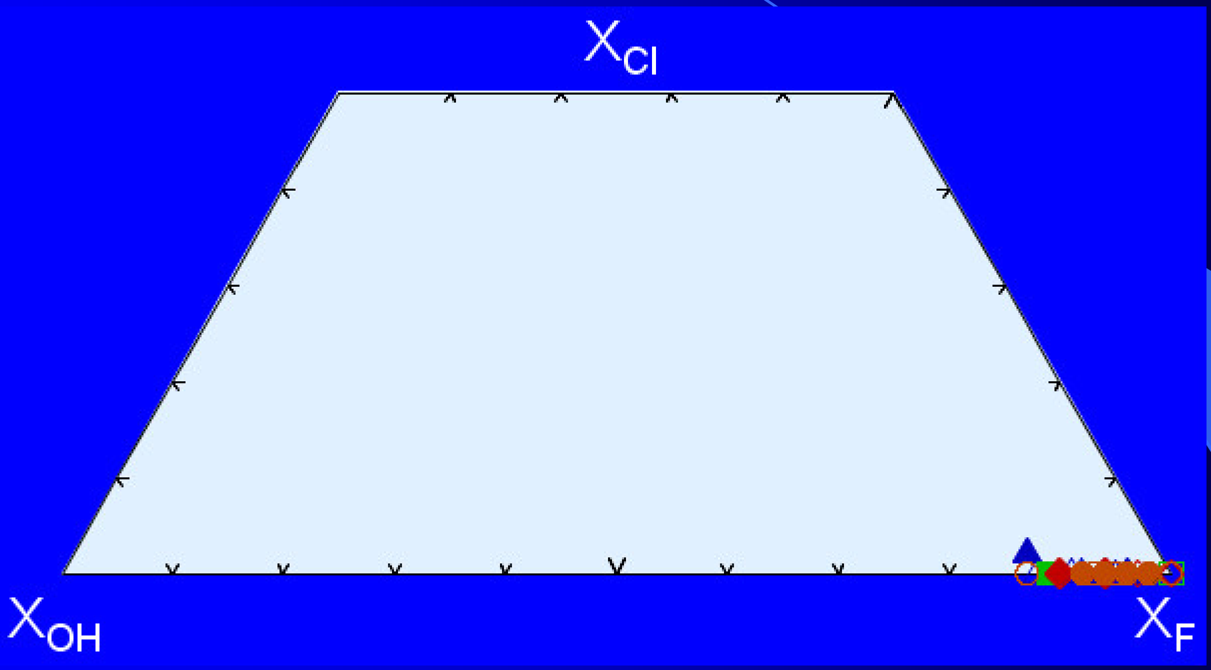


$Log(f_{H2O}/f_{HCl}) = [1000/T]*[1.15 – 0.55X_{Mg} + 0.68 – log(X_{Cl}/X_{OH})]$ (Munoz, 1992)

$Log(HCl/\Sigma Cl)^{aq} = -0.63 – 0.035P$ (MPa) Piccoli & Candela (1994)

$D_{Cl}^{aq/melt} = 0.000478P^{2.0587}$: P in MPa (Signorelli & Carroll, 2000)

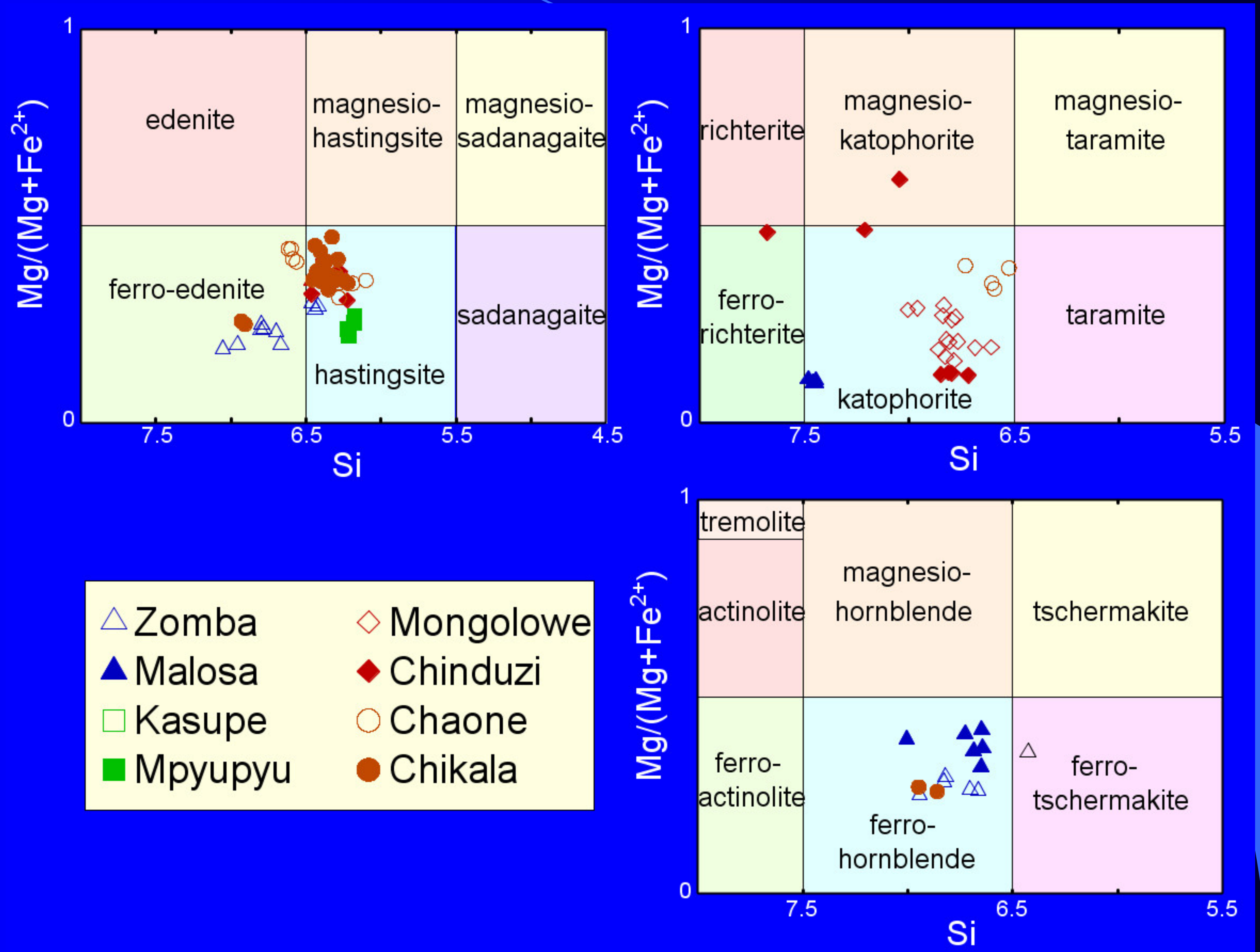
The Chilwa Apatites are Fluorapatites



For felsic magmas:

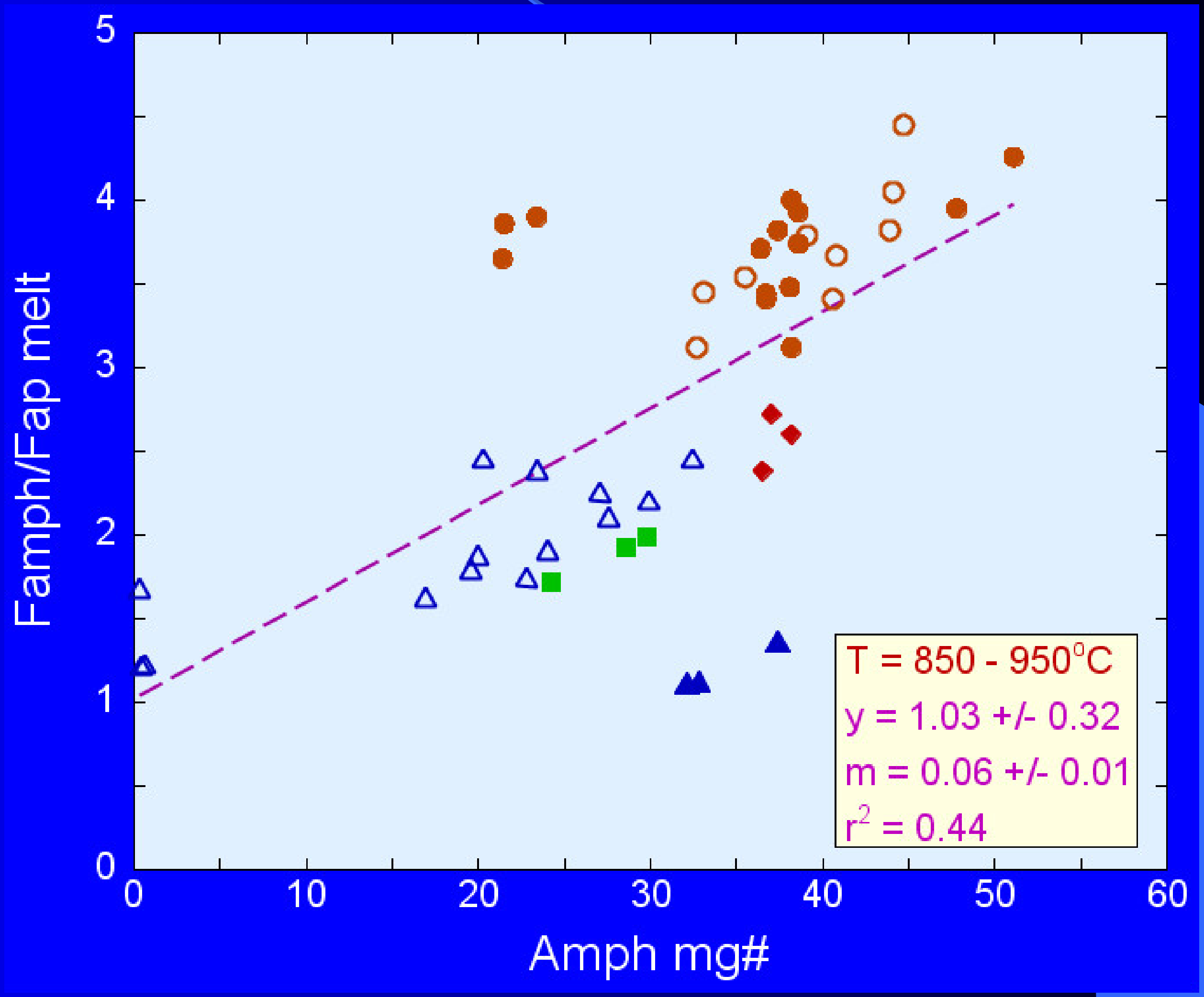
X_{Fapat} = [(3.02) x (Wt.% F in melt)] + 0.12 Webster et al. (2009)

Classification of Chilwa Amphiboles



An Empirical Model for the Partitioning of F Between Amphibole and Melt

- Melt composition calculated using apatite F concentrations.
- Apatite saturation temperatures for samples used in the calculation range from 950 to 850°C.
- Thin section observation indicates that the two minerals co-crystallized.
- Both silica-saturated and silica-undersaturated felsic rocks used in the model.



Whole-rock F and Cl Abundances

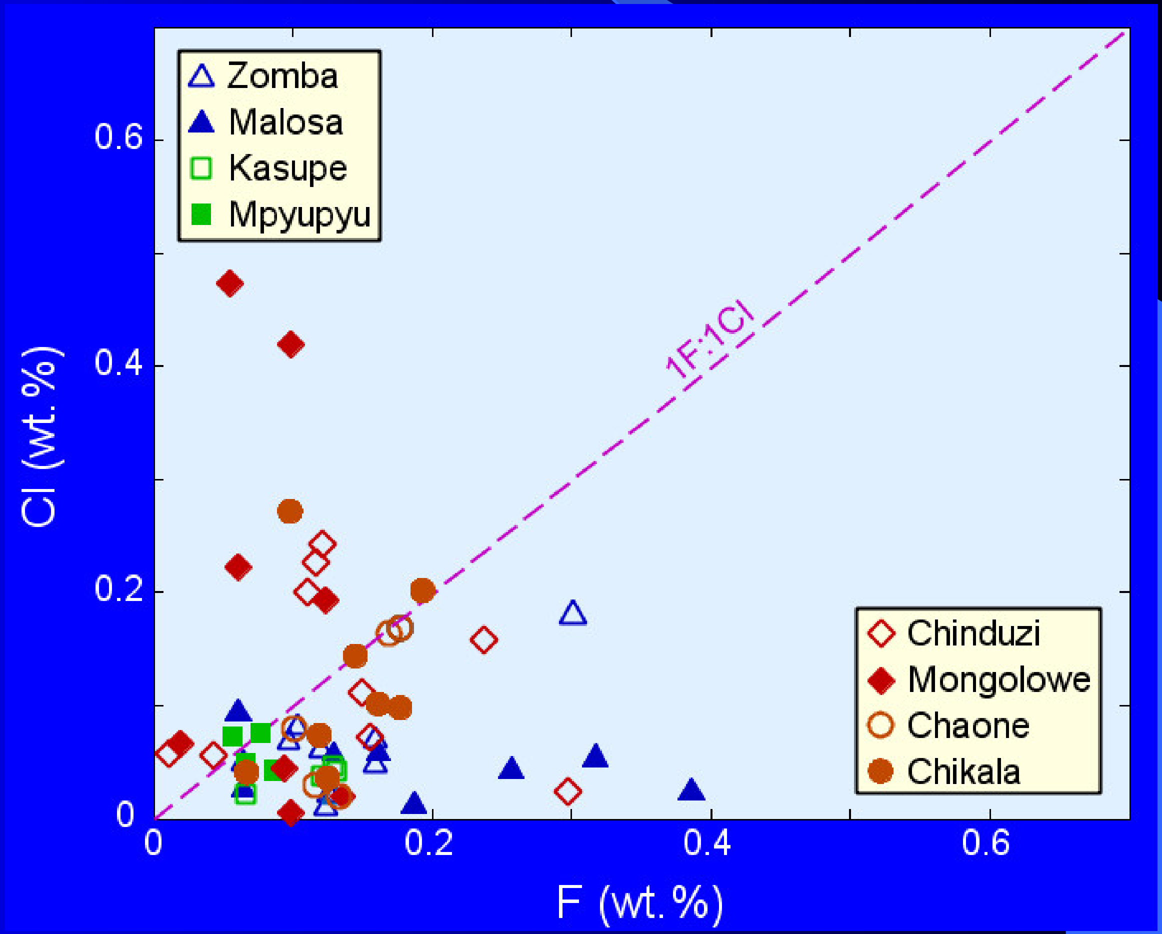
1) The silica-saturated to silica-oversaturated rocks tend to be enriched in F relative to Cl.

2) The silica-undersaturated rocks, particularly the nepheline syenites that comprise Chinduzi and Mongolowe, tend to be enriched in Cl relative to F.

3) Petrographic observation reveals that the Cl-enriched syenites often contain minor amounts of sodalite.

4) Is this sodalite precipitated from late stage solutions or is it of magmatic origin?

5) Answer later in talk.



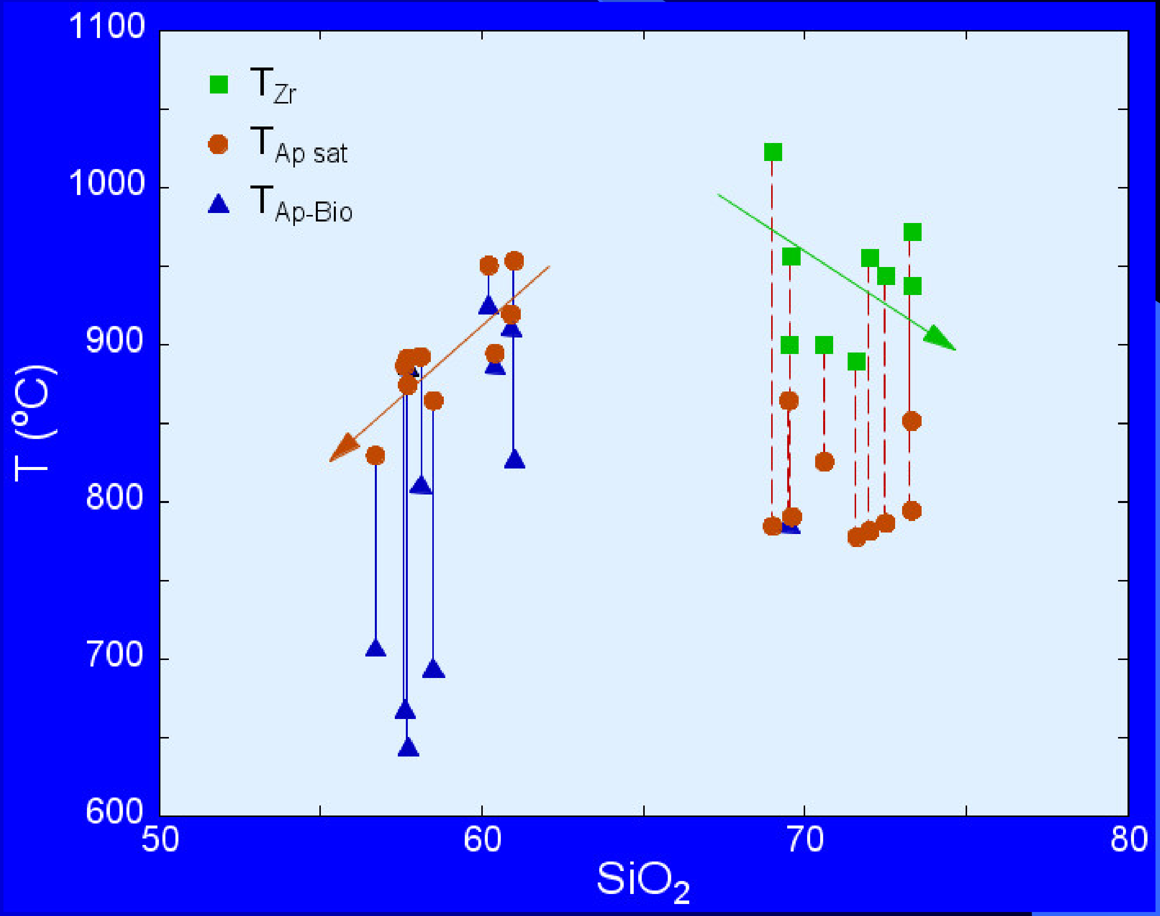
What do Geothermometers Tell Us?

Actually Quite a Bit – But Care Must be Taken in Their Application

1) The zircon saturation geothermometer should not be used outside of its calibration range, which effectively means that this geothermometer cannot be applied to alkali-rich rocks. The presence of xenocrystic zircon means the estimated temperatures are maximum T. Absence of zircon – minimum T.

2) Apatite saturation T's are less than T_{Zr}, hence apatite does not appear early in the crystallization history.

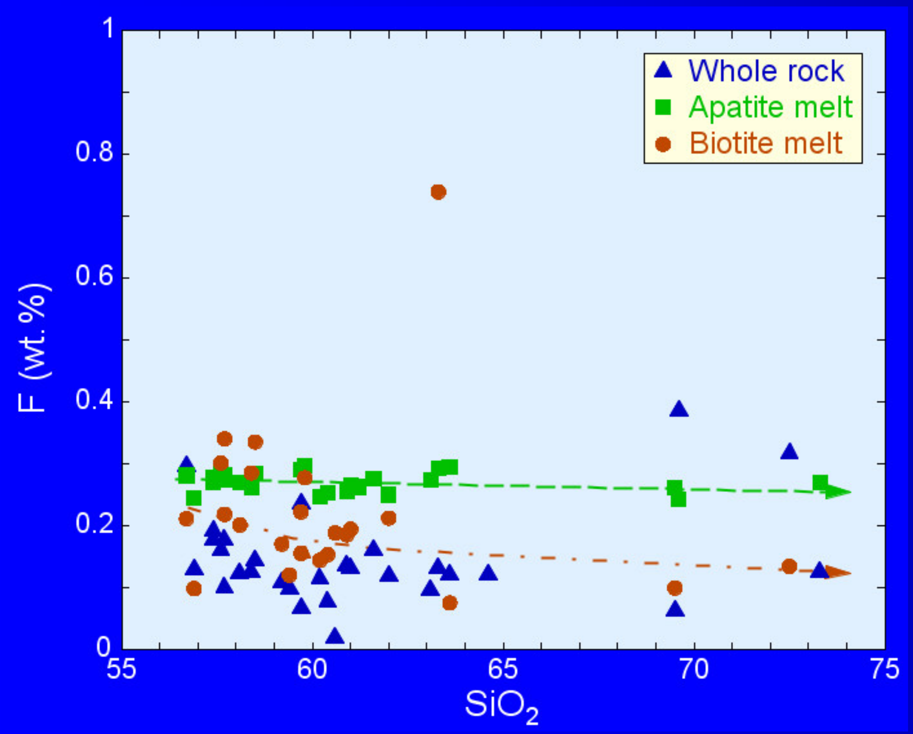
3) Generally apatite-biotite Ts are the same or less than apatite saturation Ts implying that biotite crystallizes at the same time or later than apatite. In some cases this is not an equilibrium pair.

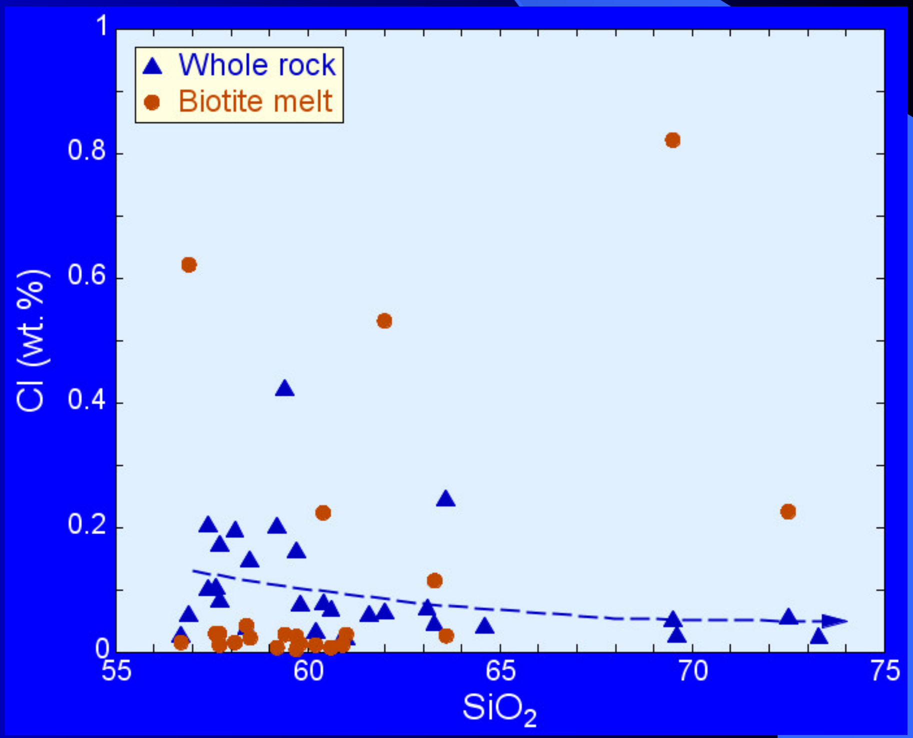


Comparisons Between F and Cl Rock Data and Melt Compositions Calculated Using Minerals

1) F – In general calculated melt concentrations are greater than those measured for the whole-rocks. Apatite calculated F is generally the same or greater than biotite calculated F which agrees with the geothermometer predictions. Both biotite and whole-rock data show a slight decrease in F with increasing SiO2.

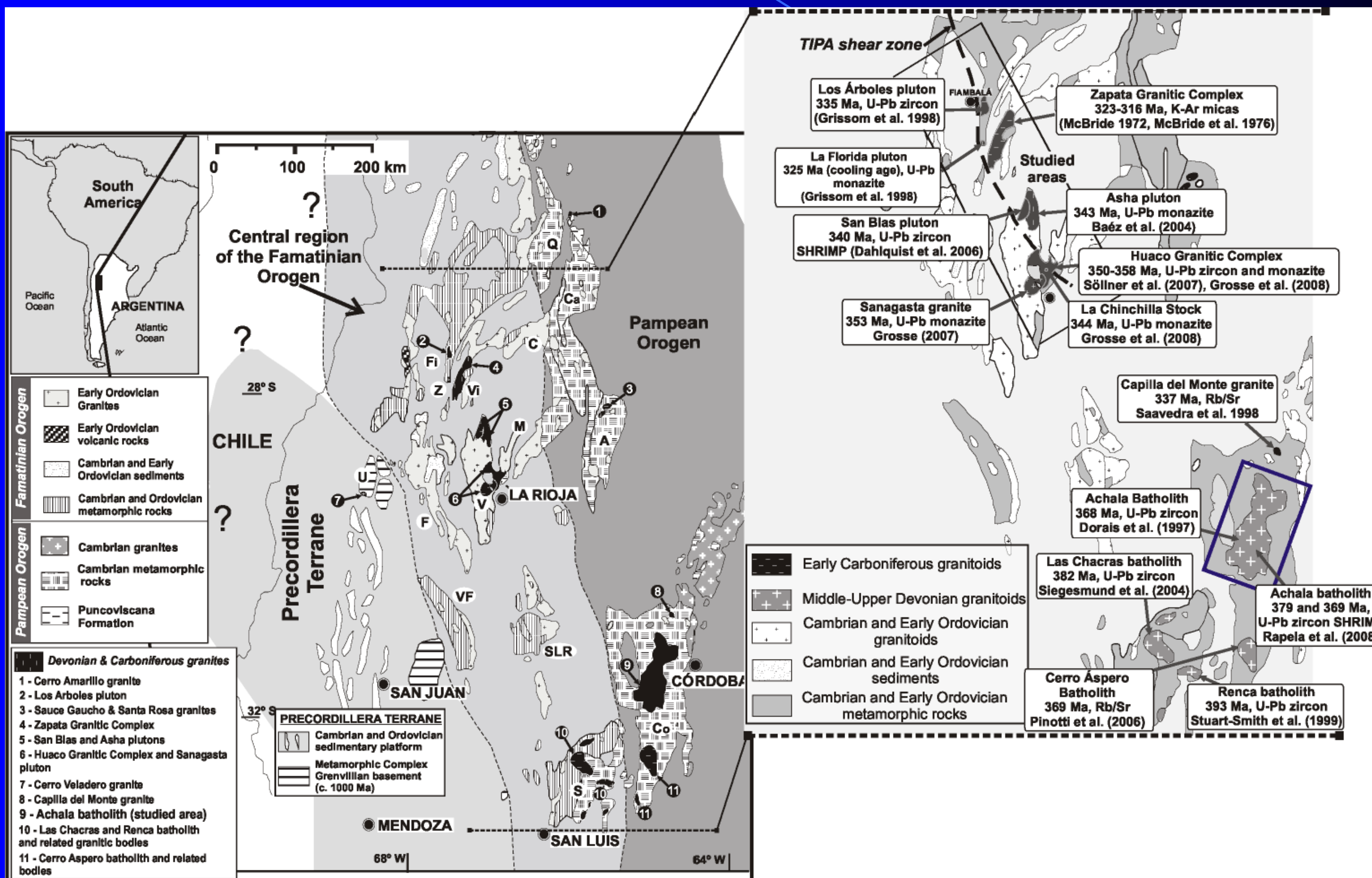
2) Cl – Does not occur in measurable quantities in apatite. In general Cl in the whole-rock is greater than that calculated using biotite. For the silica-undersaturated rocks that contain sodalite, biotites do not contain significant Cl. The few biotites that show high Cl are late stage biotites in the silica-saturated to silica-oversaturated rocks.



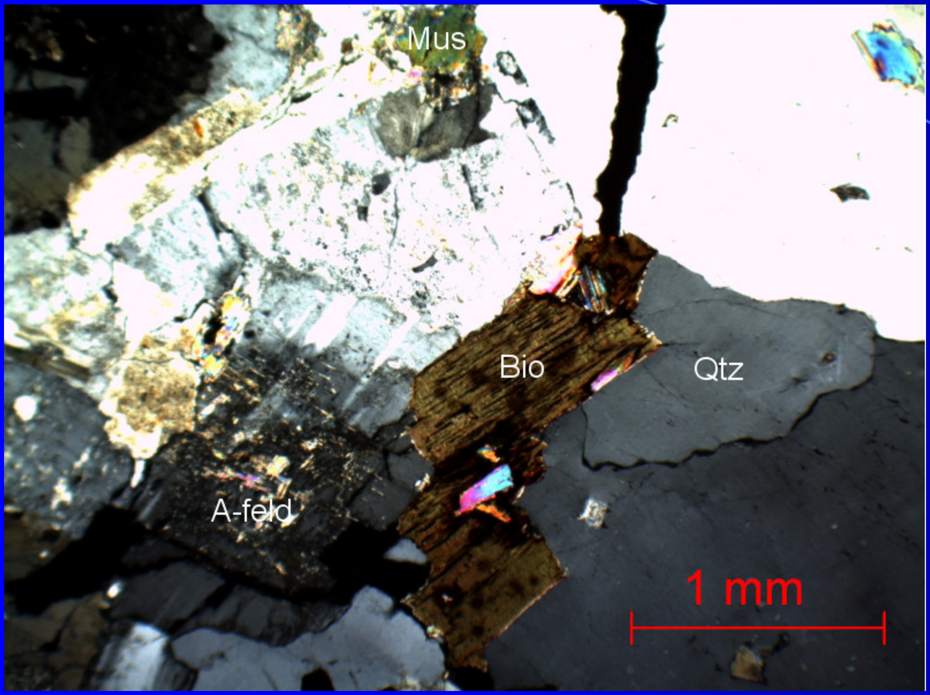


Post-Orogenic Granites in Western Argentina

These A_2 granitoids are slightly to strongly peraluminous, are associated with shear zones, and are emplaced shortly after a long period of orogenesis.



Sierra de Ancasti

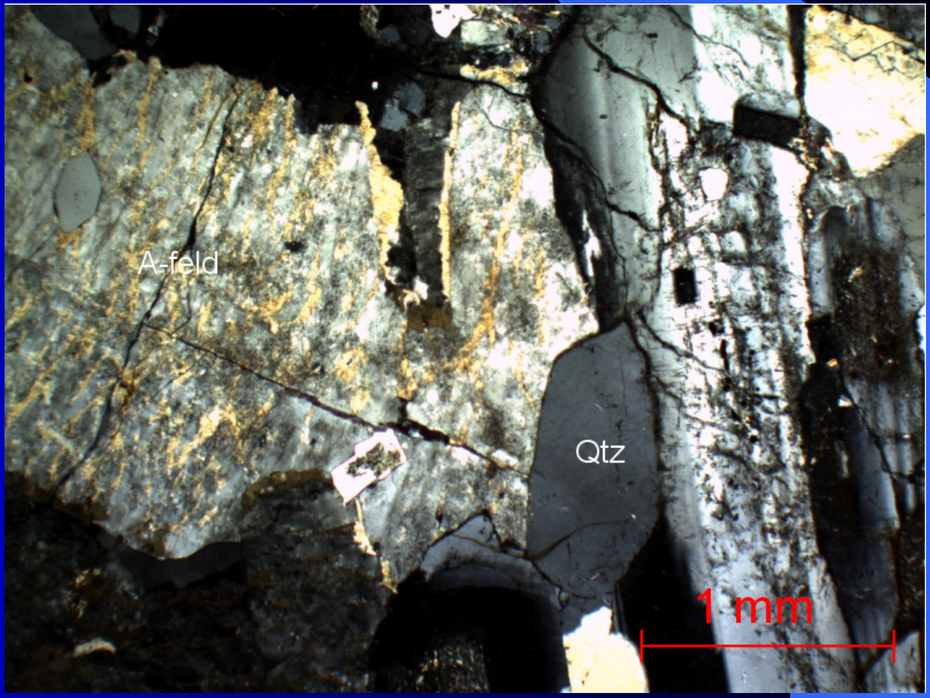


Santa Rosa pluton –

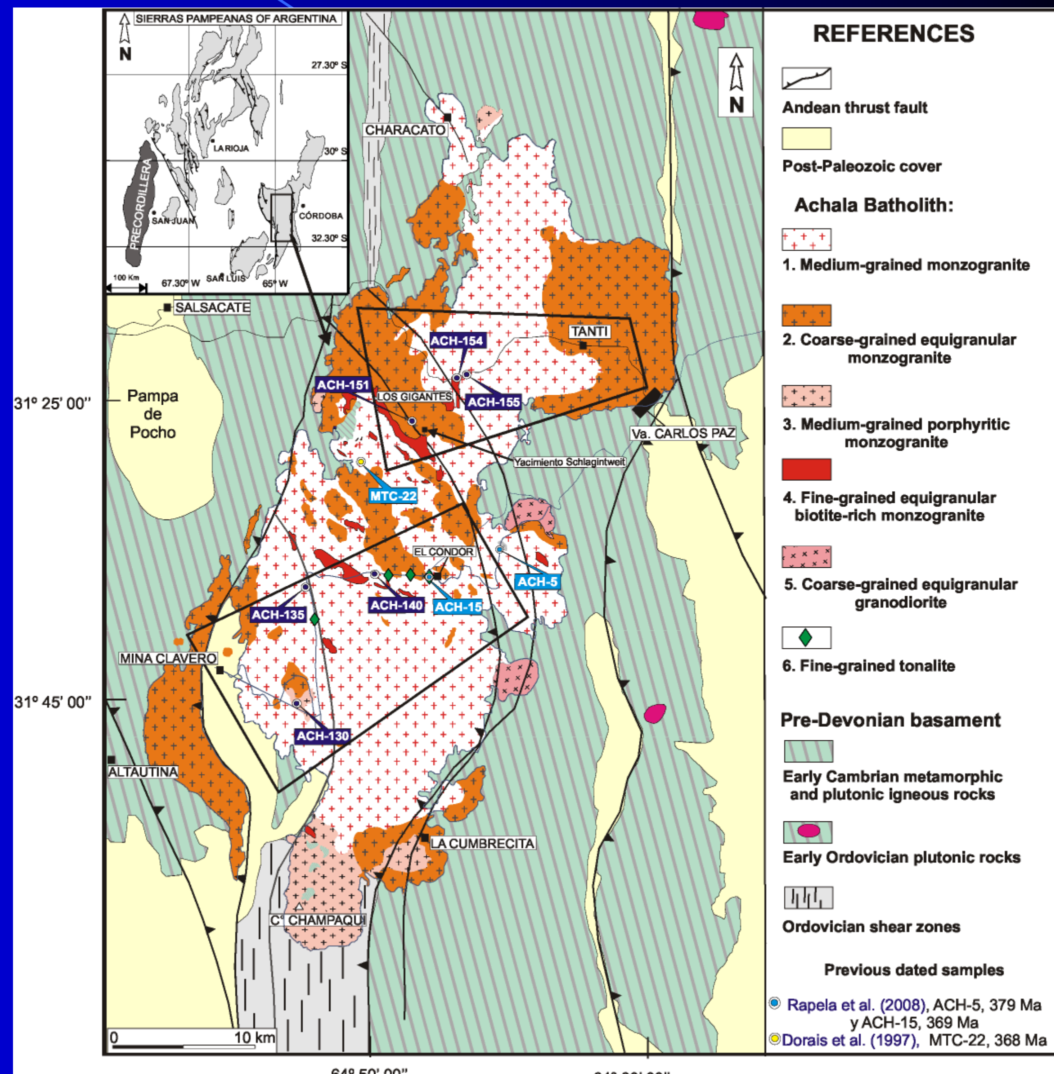
ANC122 – Porphyritic two mica (biotite>muscovite) granite. Core facies. Crossed polars.

Sauce Gaucho pluton –

ANC127 – Biotite-rich medium to coarse-grained granite. Crossed polars.



Achala Batholith



Abandoned Uranium Mine in the Achala Batholith

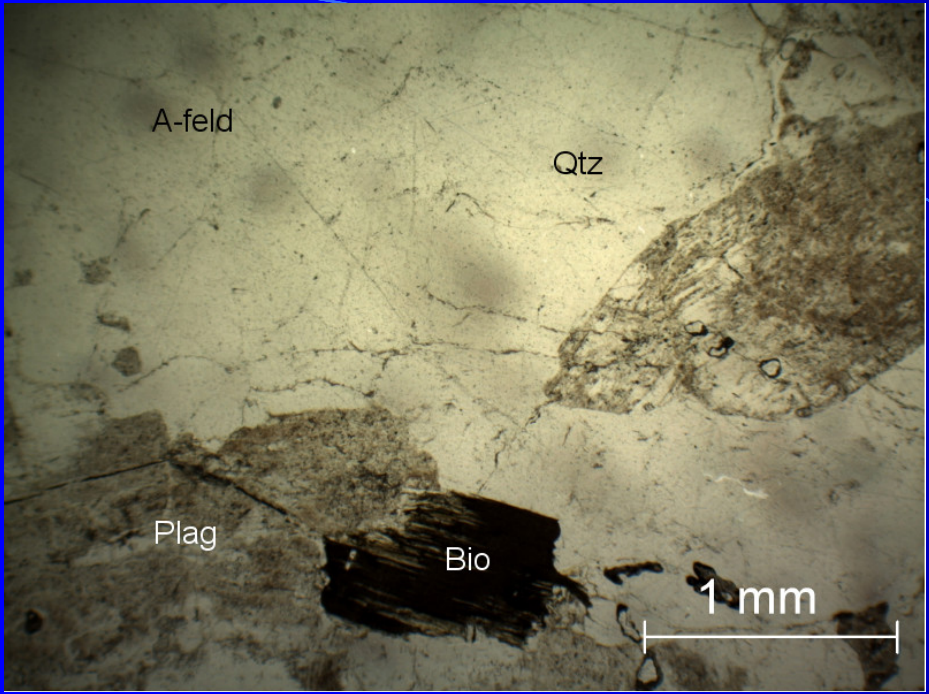
This is a sub-economic deposit opened to support the Argentina nuclear program. Currently it is not operational.

Recent geochemical work has revealed that the rocks of the Achala batholith have been extensively altered by hydrothermal solutions presumably due to a late-stage heating event (as revealed by Ar-Ar ages). This event has substantially redistributed many elements, including the so-called immobile elements.

Achala batholith

Porphyritic coarse-grained two mica (biotite>muscovite) granite. Alkali feldspar phenocrysts.

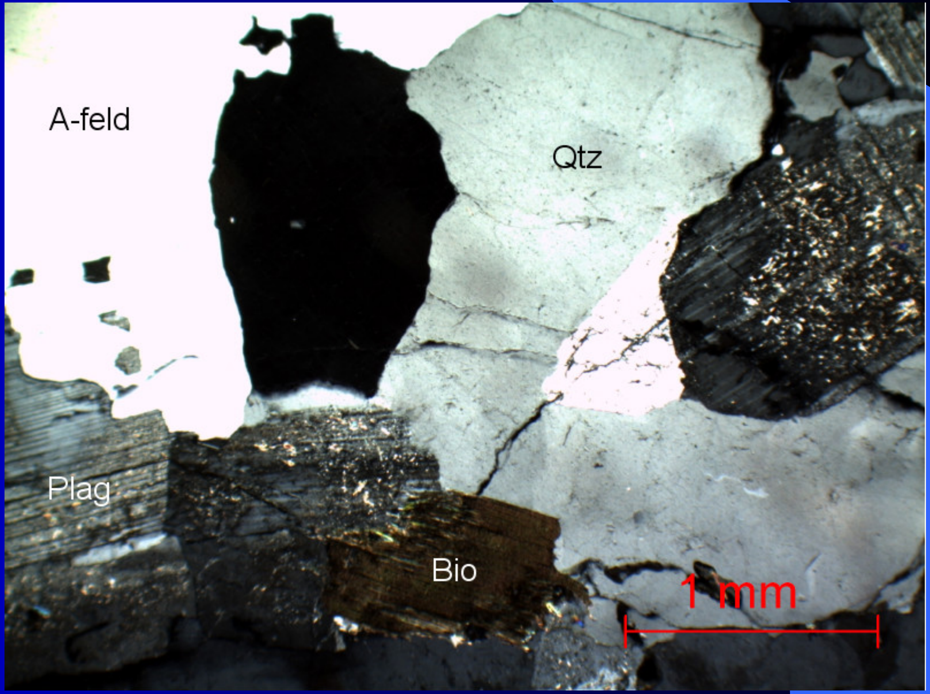
A block of fine-grained granite in the porphyritic coarse-grained granite.

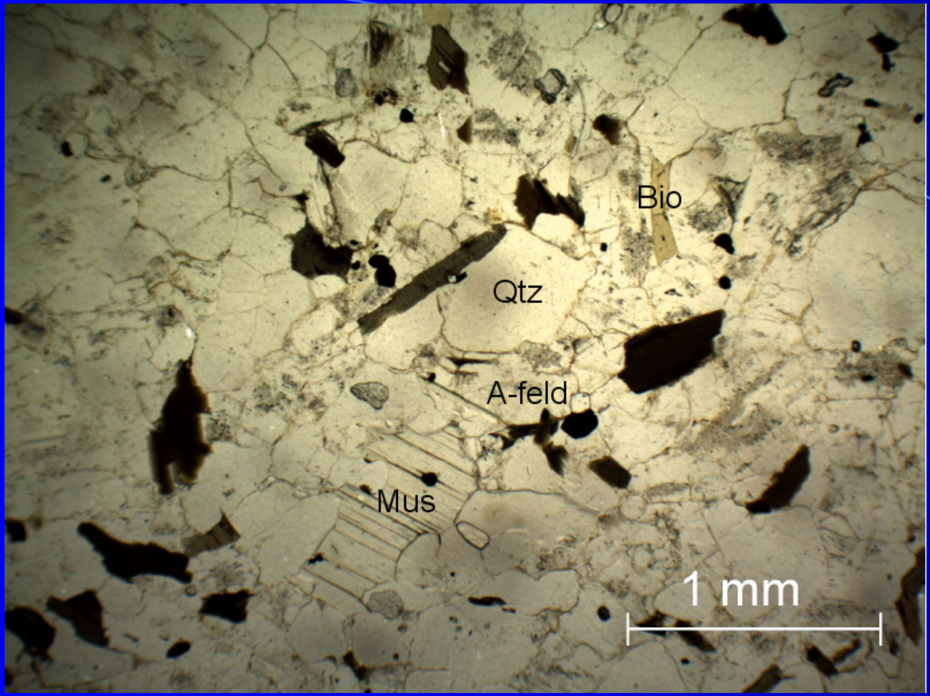


Achala batholith –

ACH151 – Porphyritic two mica (biotite>muscovite) coarse grained granite. Plane light.

Crossed polars

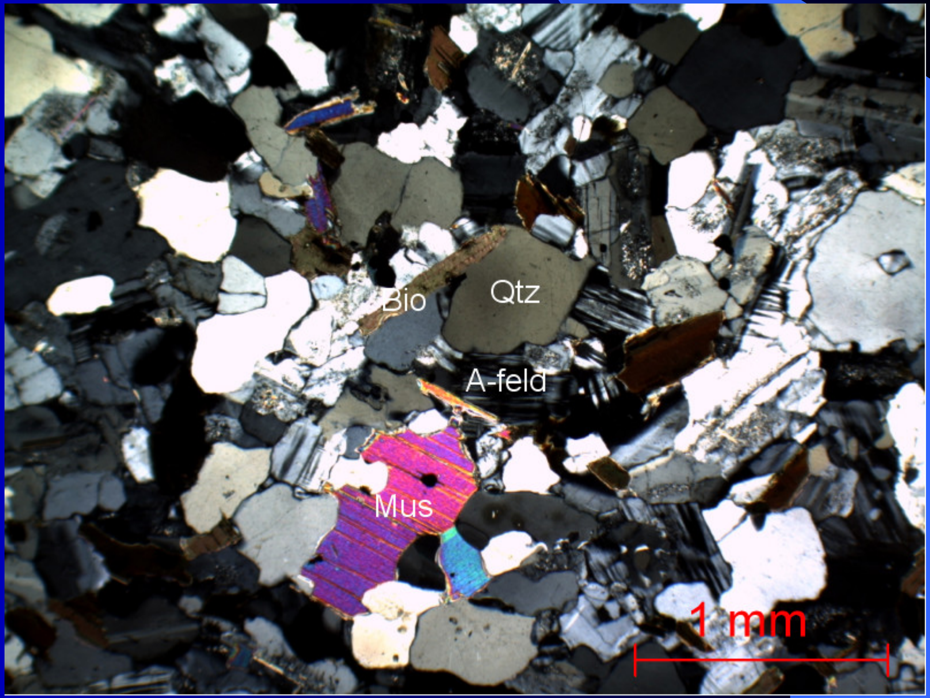




Achala batholith –

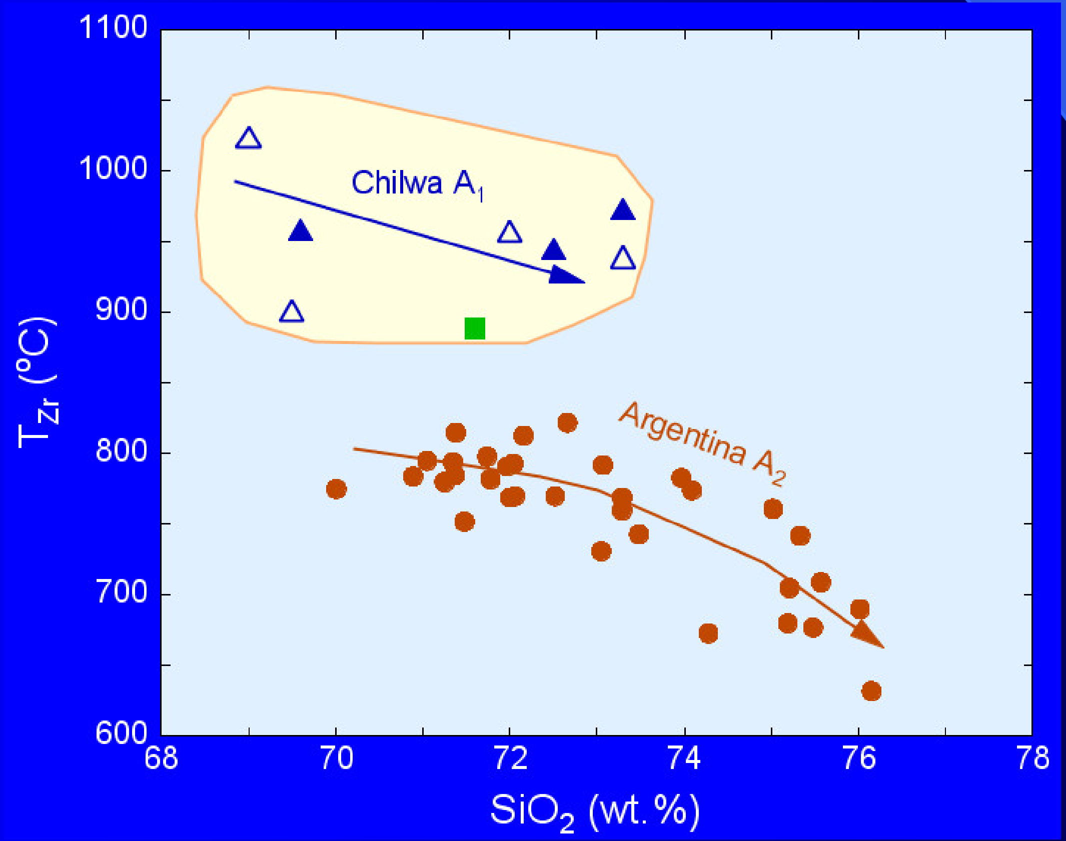
ACH154 – Equigranular biotite-rich granite. Plane light.

Crossed polars



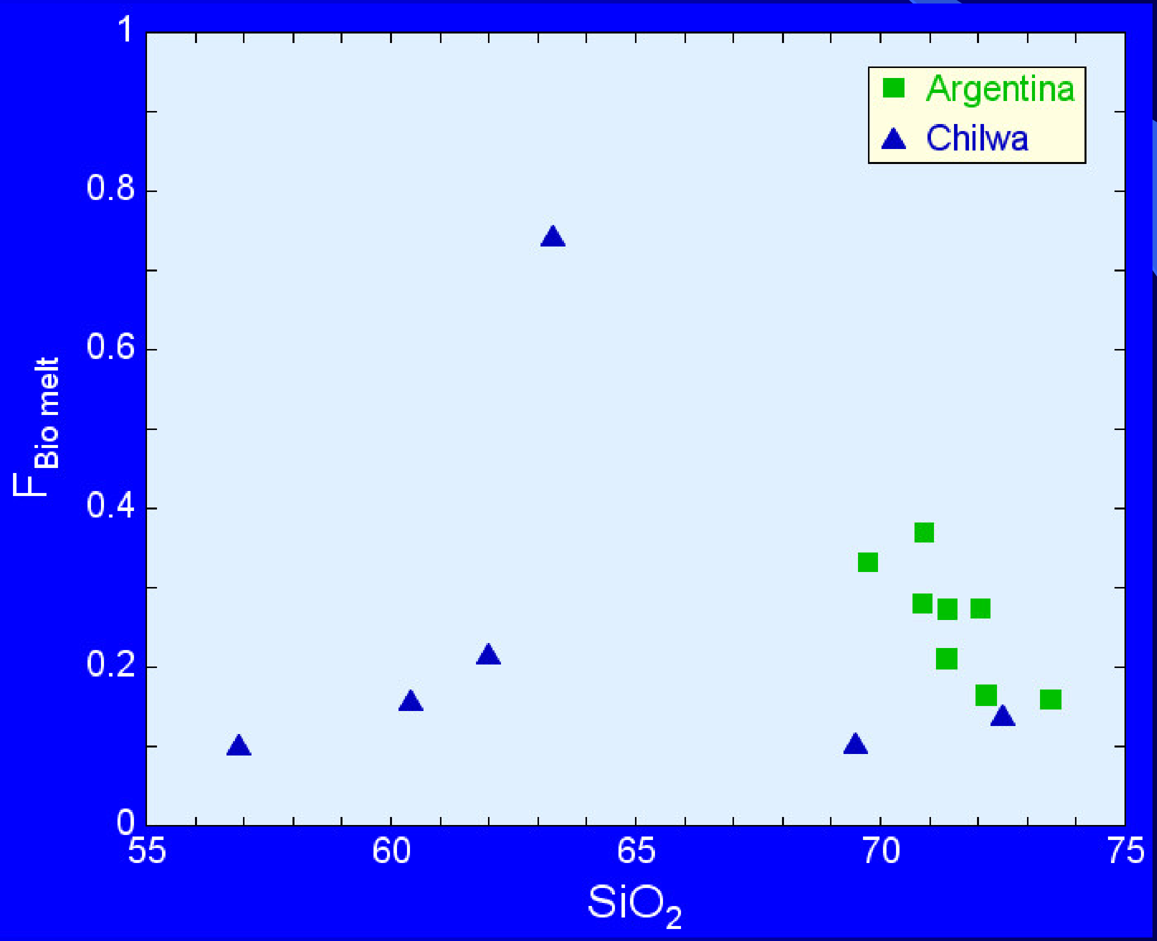
T_{Zr} for the Chilwa A_1 and Argentina A_2 granites

- Both suites show a trend of decreasing temperature with increasing SiO_2
- The temperature for the A_1 suite is approximately 150°C higher than that for the A_2 suite.
- The A_1 suite is inferred to be the result of differentiation (AFC) of a mafic magma while the A_2 suite is inferred to result from the partial melting of meta-pelites and meta-graywackes due to the intrusion of basaltic magmas.



Comparison of F Content for A_1 and A_2 Granites Based on Biotite

- F in high silica Chilwa A_1 granitoids less than in low silica granitoids.
- Argentina A_2 granitoids show a decrease in F with increasing silica. The magma is saturated with respect to apatite.
- The A_2 granitoids are enriched in F with respect to the A_1 granitoids.



Some Conclusions (Thoughts)

- The Munoz model appears to be the best for estimating F and Cl melt concentrations from biotite chemistry.
- For bioite-based calculations the temperature (and for Cl, pressure) of the system is important and should be determined.
- Different halogen containing minerals form at different times and therefore show a variation in halogen content with crystallization.
- No model currently exists for using amphibole to determine halogen magmatic chemistry. The empirical model developed here should be applicable, with appropriate caveats, to felsic systems.
- For the two A-type granites investigated in this study, the melts do not appear to have excessively high F concentrations.
- When used with caution the available geothermometers for felsic systems can potentially yield important data for understanding the variation of F and Cl in the magmas and the evolution of the magmatic system.