

Optical microscopy of cement clinker

- Clinker Microscopy
- The Ono Method
- Examination of polished sections

Clinker Microscopy

- Introduction
 - Clinker microscopy
 - Transmitted light microscopy uses a light source below the sample so that light which passes through the sample is examined
 - Reflected light microscopy uses a light source above the sample which shines on a polished section, usually etched to differentiate between different minerals



The Ono Method

- Ono's method
 - Designed as a means of on-site control of the kiln. Samples of ground clinker are examined using transmitted light microscopy to measure four basic parameters which are used as a guide to the quality of the clinker.
 - The samples are examined as powders in a liquid of known refractive index. The parameters are:
 - Size of alite.
 - Birefringence of alite,
 - Size of belite.
 - Colour of belite.

The Ono Method

- **Size of alite.**
- Birefringence of alite.
- Size of belite.
- Colour of belite.

Size of alite

- In the Ono method the size of alite refers to the most commonly occurring size, or the mode. This is judged subjectively then ten selected crystals are measured and the average is quoted.
- According to Ono, alite size depends on the burning rate and the crystallisation rate. Quick burning by a short flame produces small crystals, slow burning in a long flame produces large crystals.

Other factors affecting alite size

Process	Effect of increase on alite crystal size
Burning zone temperature	Coarser
Secondary air Temperature	Coarser
Cooler grate speed	Finer
% Front end fuel	Finer
Kiln feed rate	Finer
Chemistry	
Alite iron content	Finer
Alite aluminium content	Finer
Aluminate iron content	Finer
Aluminate aluminium content	Coarser

The Ono Method

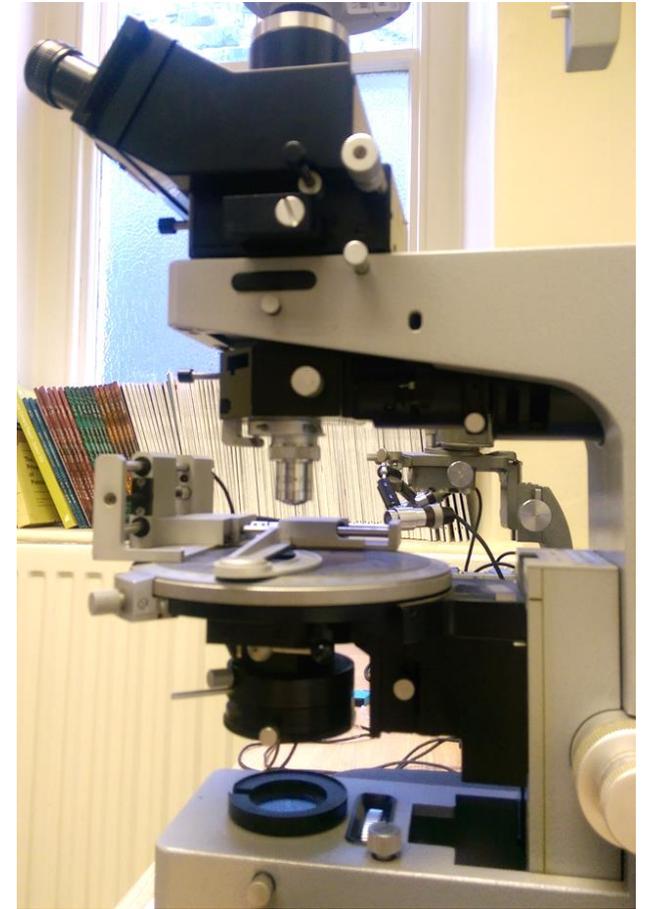
- Size of alite.
- **Birefringence of alite.**
- Size of belite.
- Colour of belite.

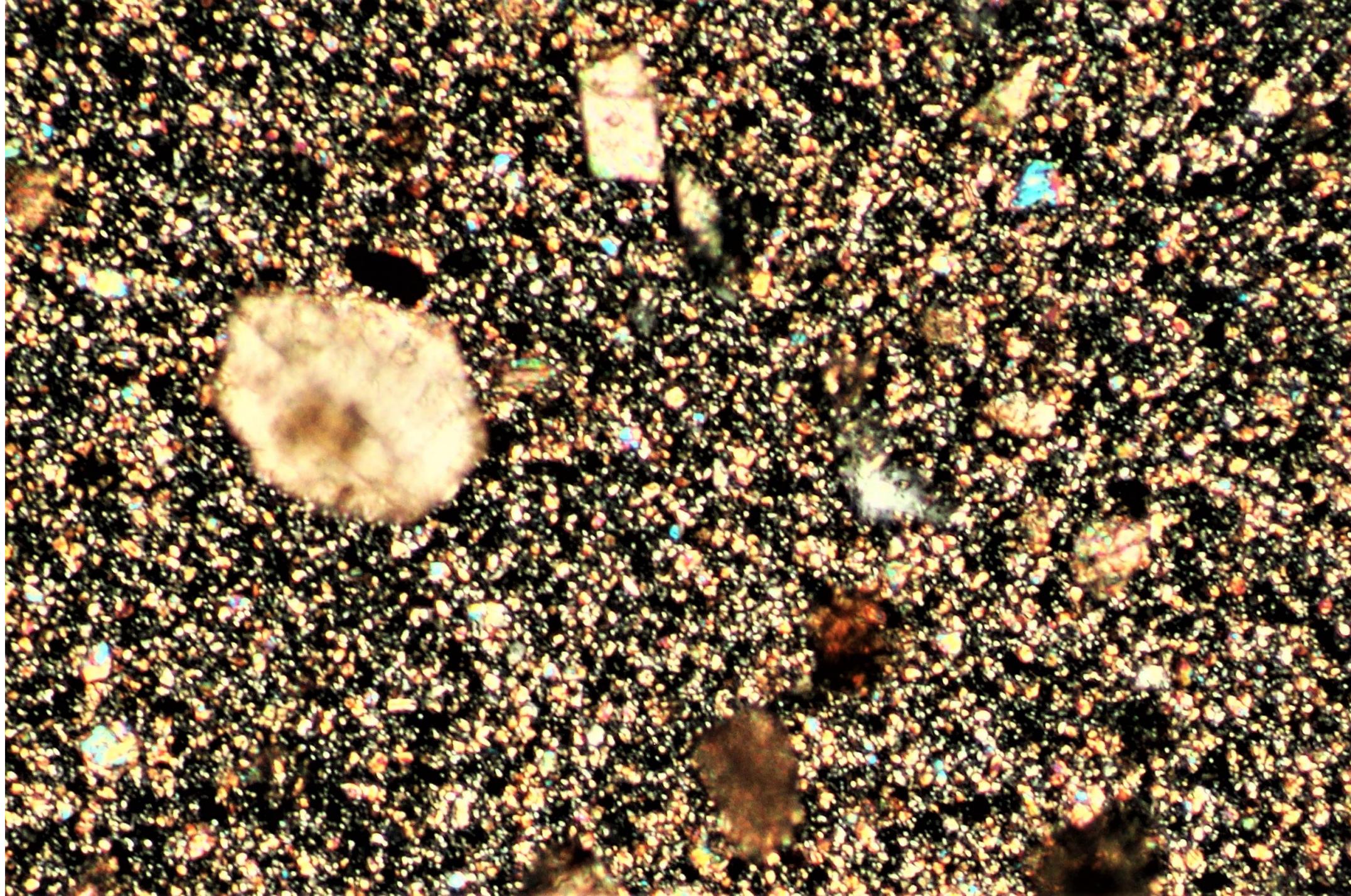
Birefringence

- Birefringence is a property of crystals concerning the manner in which light passes through them. Light is refracted when passing through a medium other than air and the index of refraction is the velocity of light in the medium relative to the velocity in air.
- The structure of the crystal can give a range of indices of refraction and in anisotropic crystals there are two indices, corresponding to the 'fast' light ray and the 'slow' light ray. The difference between these two rays is known as birefringence and can be measured relatively easily using optical methods involving cross polarised light.

Birefringence

- To use cross polarised light a beam of white light is shone from the base of the microscope through a polarising filter which will only allow light vibrating in one plane.
- This light then passes through the transparent crystals in the sample after which it is passed through another filter, known as the analyser, which will only allow light vibrating in a plane at right angles to the first filter.
- If the crystal has not affected the light direction then the field will be black as no light can have passed through. However, if the crystal has refracted the light away from the plane of the polariser then some can pass through.
- In the case of double refraction there will be two beams passing through the analyser which be out of phase having travelled different path lengths through the crystal and which produce interference colours, the colour depending on the birefringence of the crystal.





Birefringence of alite

- The birefringence of alite varies depending on the crystal modification of the alite as it emerges from the kiln.
- Rhombohedral (R) alite has a birefringence of 0.007 to 0.01, Disordered M1 alite still contains some R and has a birefringence of 0.005 to 0.007 and M3 alite has similar birefringence. Triclinic alite has a birefringence of less than 0.004

C₃S on cooling

Reducing temperature

Rhombohedral C₃S



Monoclinic M3 C₃S



Monoclinic M1 C₃S



Triclinic T2 C₃S

All C₃S forms in the BZ as Rhombohedral

Stabilised by high MgO. Fine, euhedral crystals

Inversion to M1 encouraged by high SO₃, which encourages coarse, irregular crystals with few inclusions.

Occurs rarely in slowly cooled, pure crystals

The Ono Method

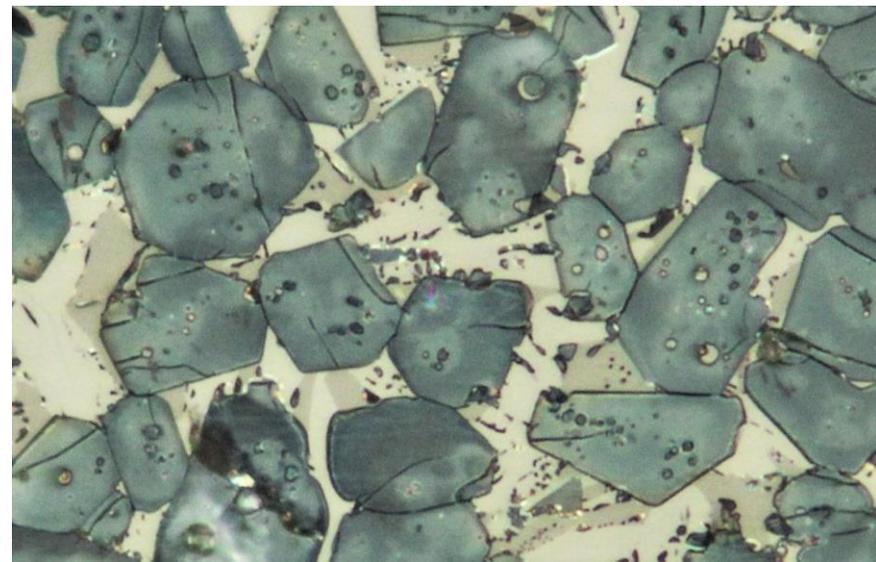
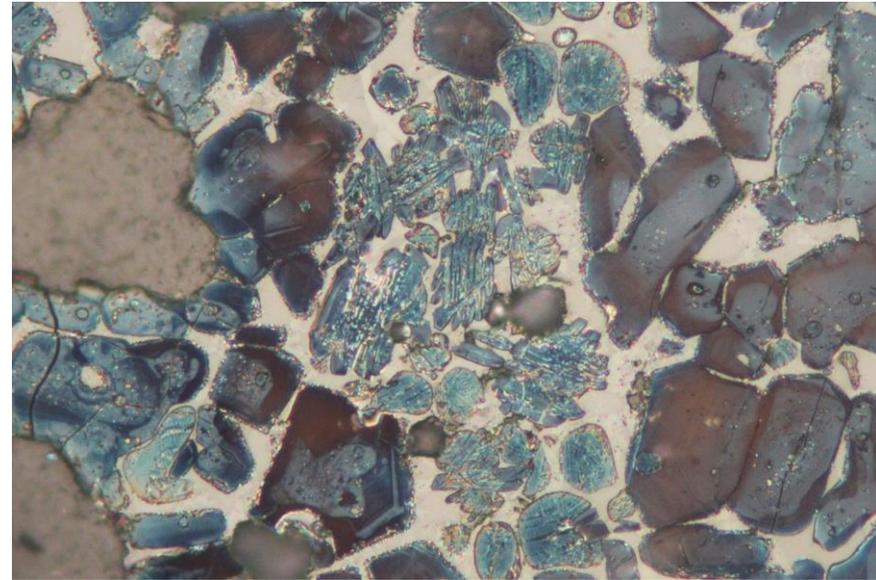
- Size of alite.
- Birefringence of alite.
- **Size of belite.**
- Colour of belite.

Size of belite

- For Ono the belite size is measured in a similar manner to the alite, taking the average of ten crystals selected as being of the most commonly occurring size.
- As with alite the belite crystals occur in a number of phase modifications at different temperatures. They are formed as small crystals known as alpha prime (α') which convert to α above 1400°C and grow quite rapidly. The size of most of the belites therefore depends on the length of time the clinker is above 1400°C.

Other factors affecting belite size

- Amount of coarse silica present in the kiln feed.
- Degree of decomposition of belite on cooling.
- Amount of secondary belite produced on cooling.



The Ono Method

- Size of alite.
- Birefringence of alite.
- Size of belite.
- **Colour of belite.**

Belite colour

- The assessment of belite colour is made in order to relate this to the cooling rate of the clinker. The highest temperature form, α , can contain several percent of Al_2O_3 , Fe_2O_3 and alkali. However, the lower temperature forms, α' and β , can only hold a small amount.
- On cooling and phase change, therefore, the impurities are exsolved and cause a clouding of the crystals.
- When using polished sections an alternative method of assessing the cooling rate is to measure the crystals which were liquid in the burning zone, C_3A and C_4AF . The slower the cooling rate, the larger the crystals.

The Ono Method

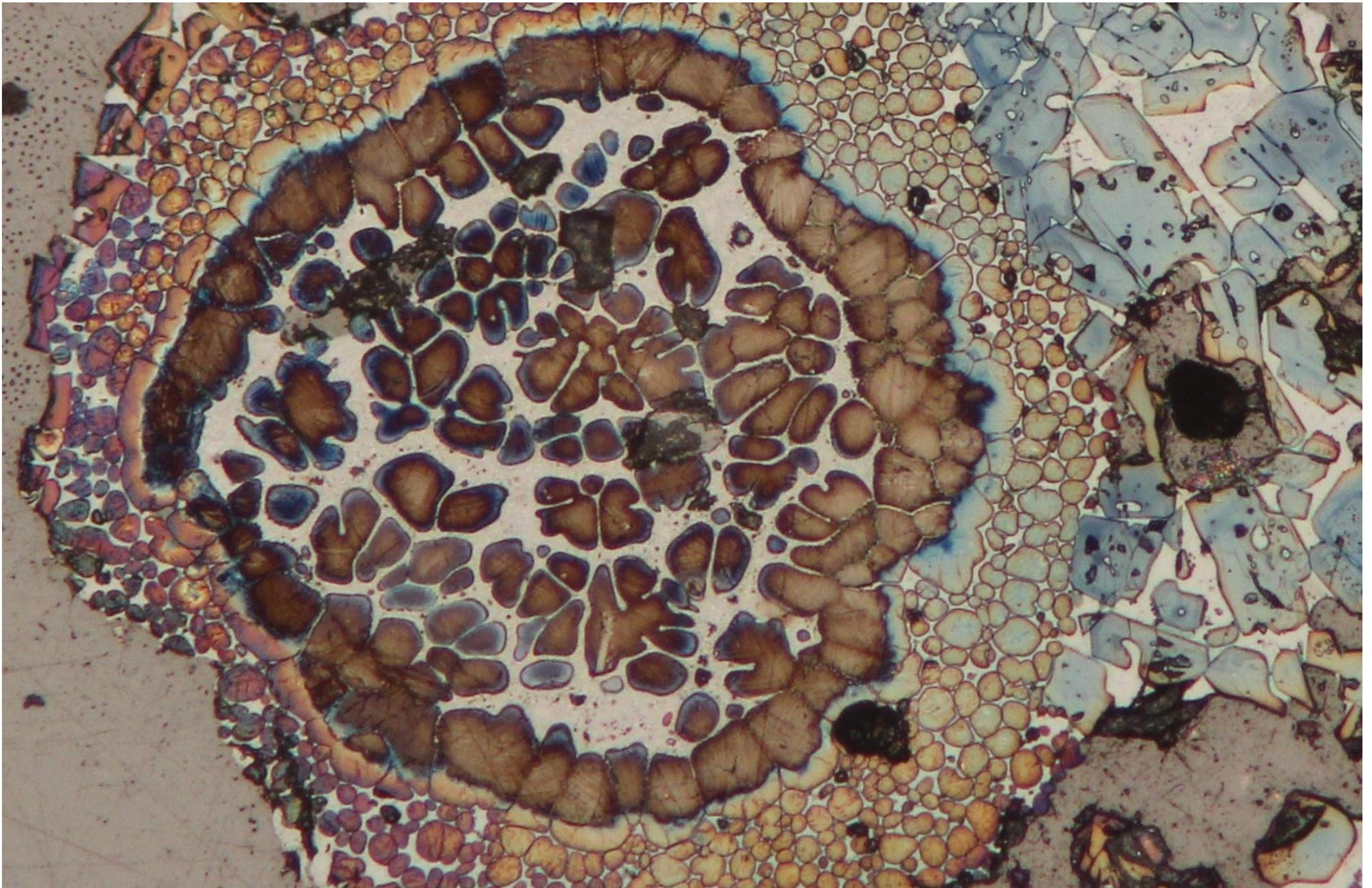
Burning condition	Hydraulic activity			
	4 Excellent (+)	3 Good (VV)	2 Average (v)	1 poor (-)
Heating rate Size of alite (μ)	Quick 15-20	— 20-30	— (25) 30-40	Slow 40-60 (120)
Maximum Temperature Birefringence of alite	High 0.010 – 0.008	— 0.007 – 0.006	— 0.006 – 0.005	Low 0.002
Burning time Size of belite (μ)	Long (20) 25 – 40 (60)	— (15) 20-25	— (10) 15-20	Short 5-10
Cooling rate colour of belite	Quick Clear (C)	— Faint yellow (FY)	— Yellow (Y)	Slow Amber (A)
Birefringence of belite	0.012	0.015	0.017	0.018
Content of alpha	Abundant (40%)	Medium (20%)	Few (10%)	Nil (0%)

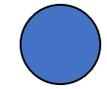
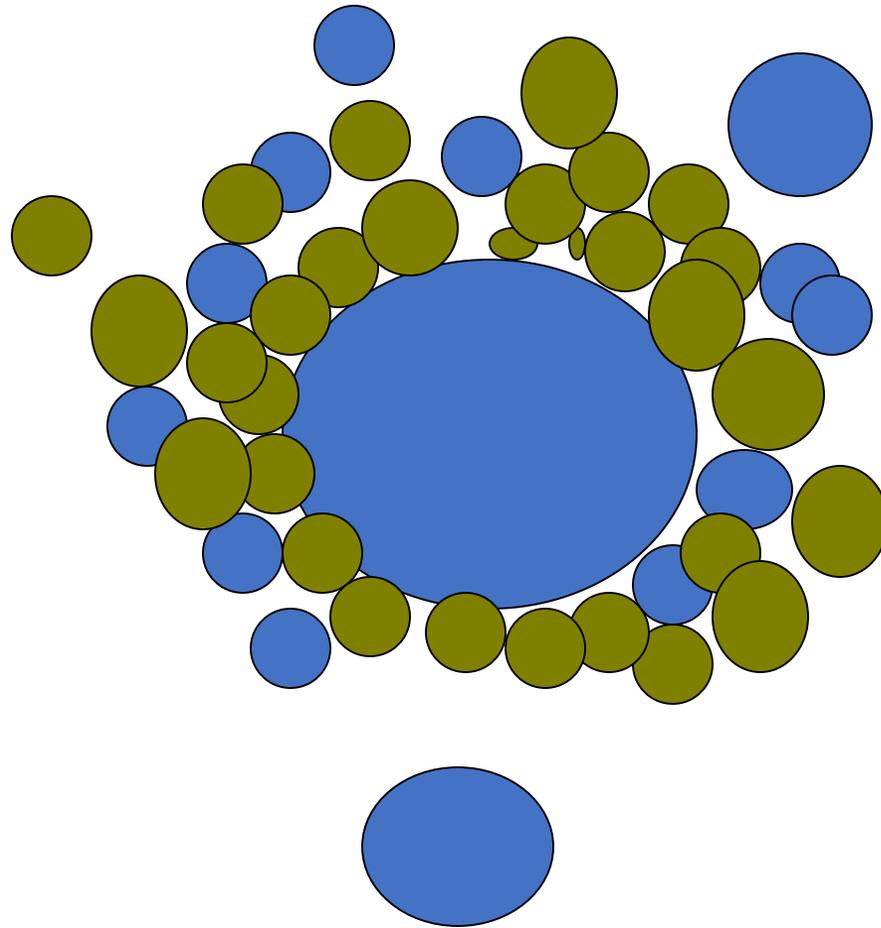
The Ono Method

- The Ono method in its simplest form concentrated only on the silicates in the clinker and allowed a rapid assessment of the state of the process.
- Ono recommended that the data should be supplemented by other methods notably the use of polished sections

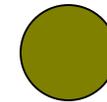
Examination of polished sections

- One of the main advantages of using polished sections rather than powders made from the clinker is that the structure of the clinker nodule is preserved and the reasons for differences in crystal sizes or cooling rates can be deduced.
- The following slides are examples of some of the most common structures found in clinkers.

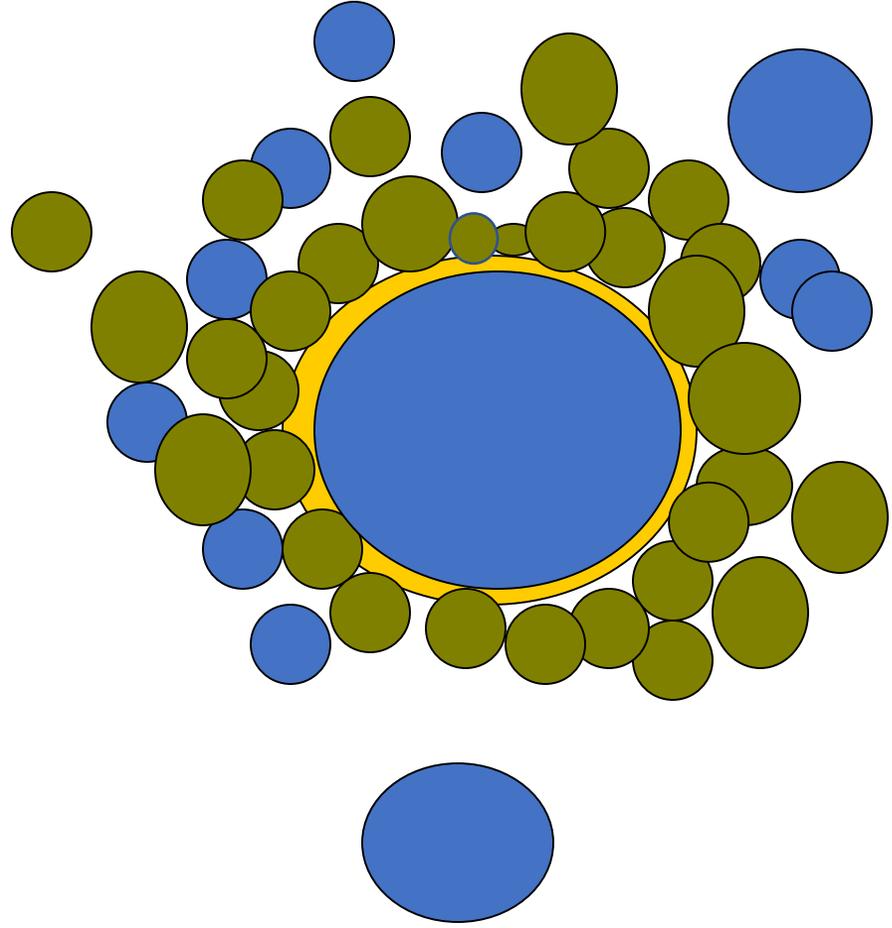




sand



limestone



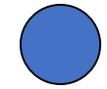
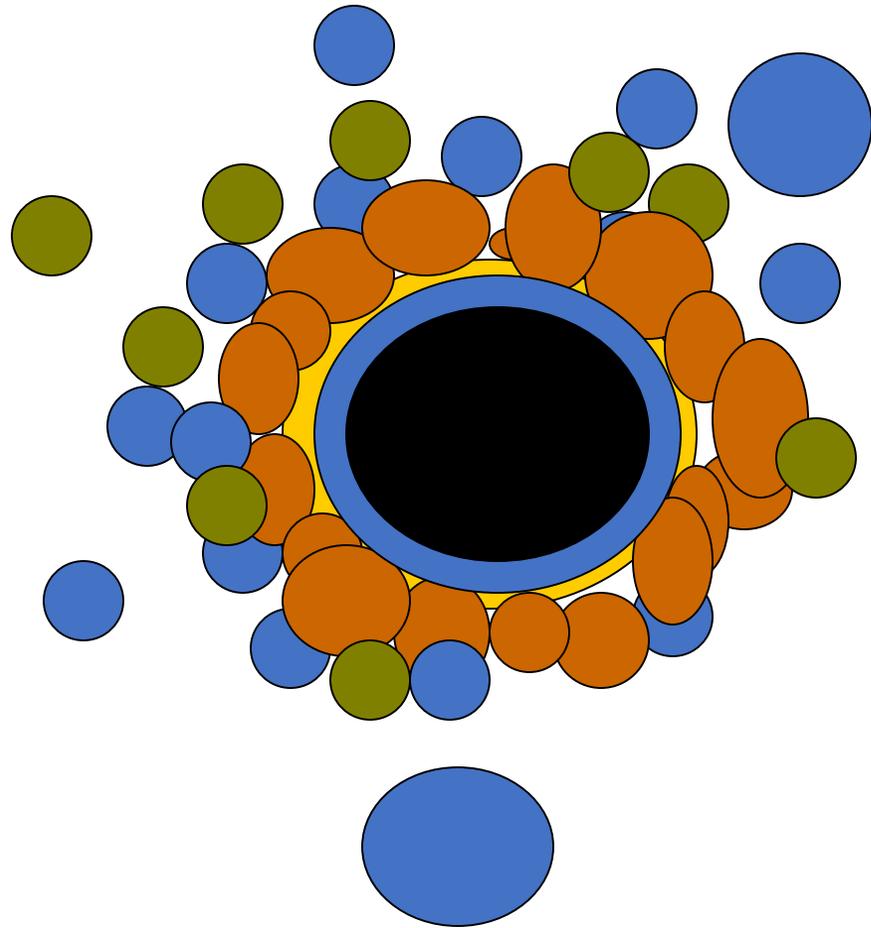
sand



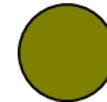
Limestone



Liquid



Sand



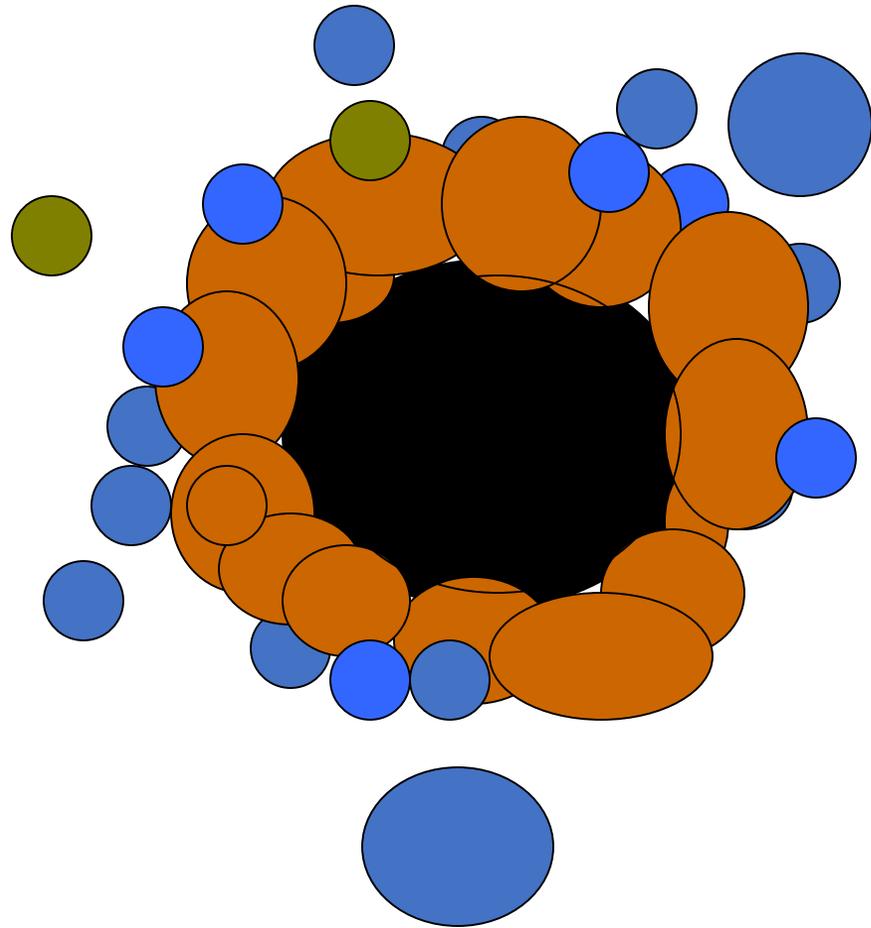
Limestone



Liquid



Belite



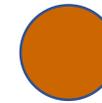
Sand



Limestone

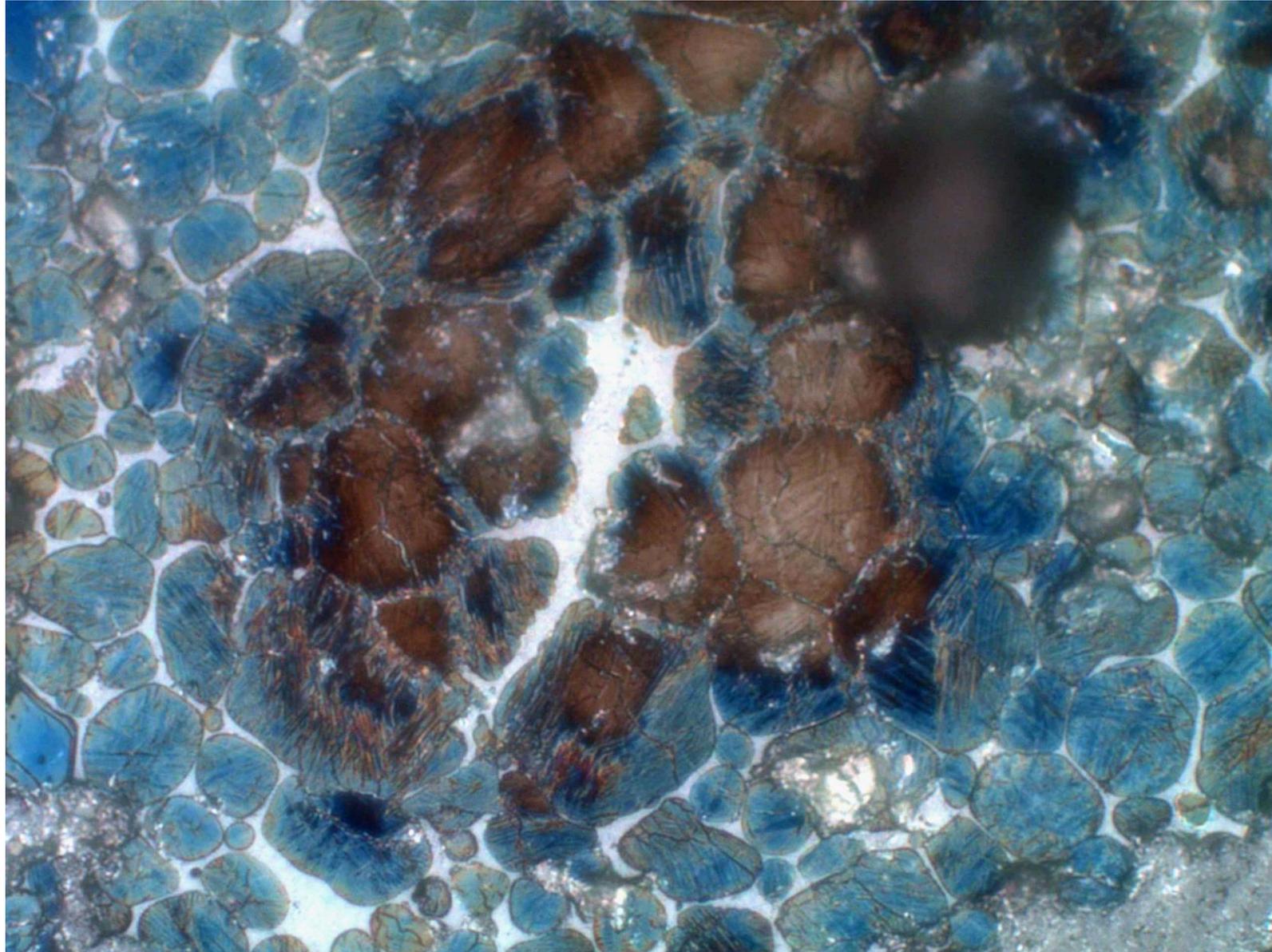


Liquid

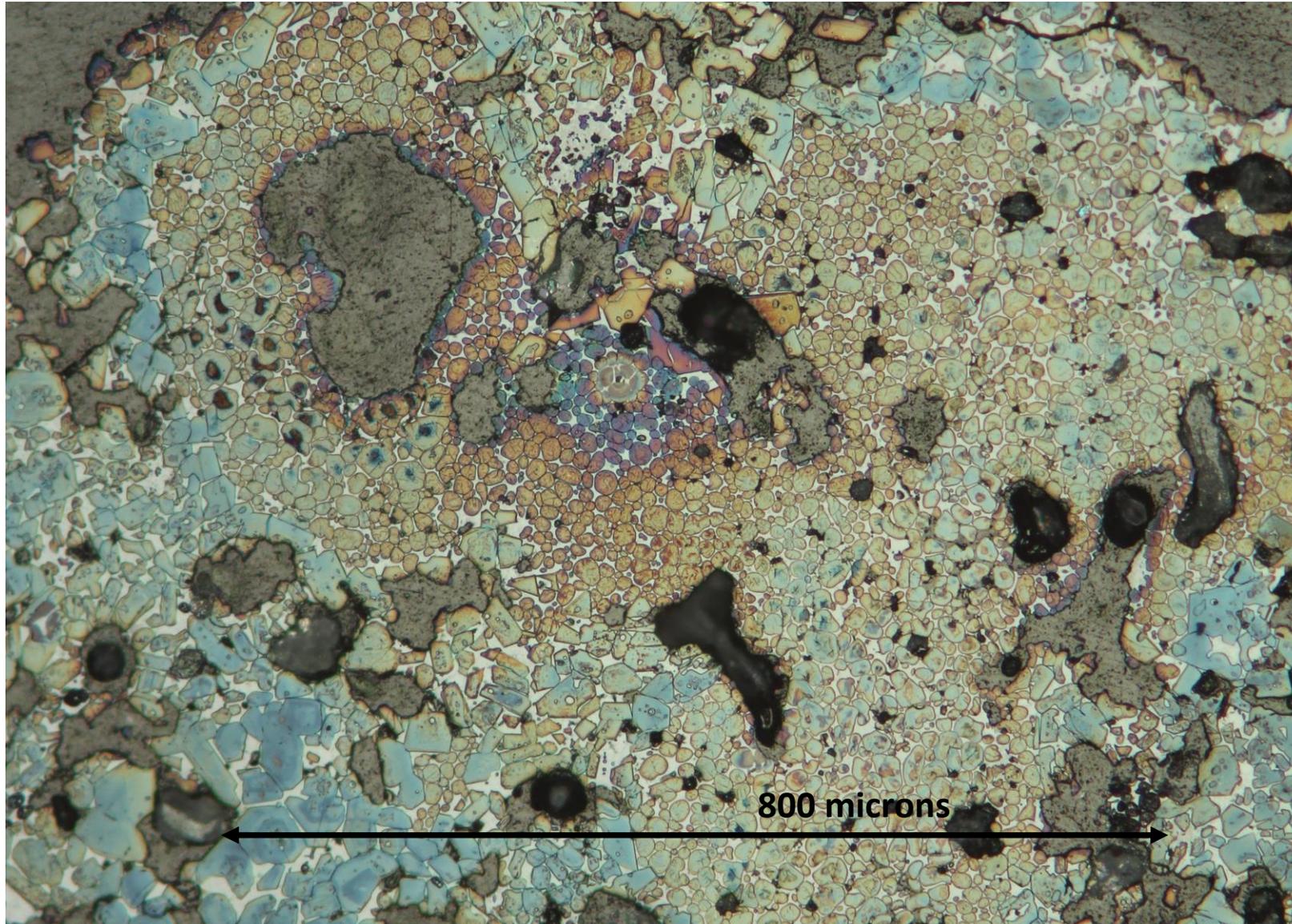


Belite

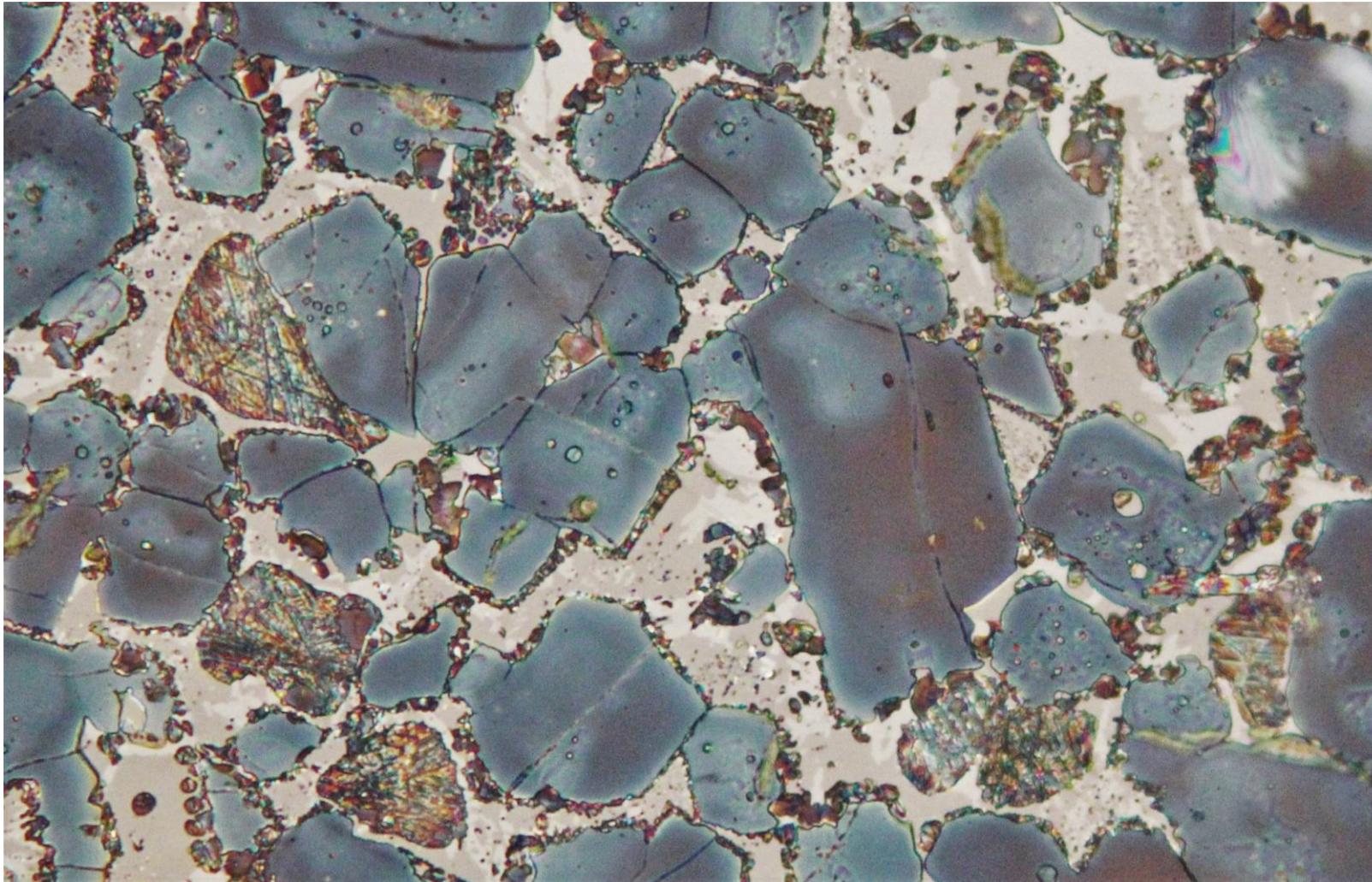
Effect of Coarse Sand Grain



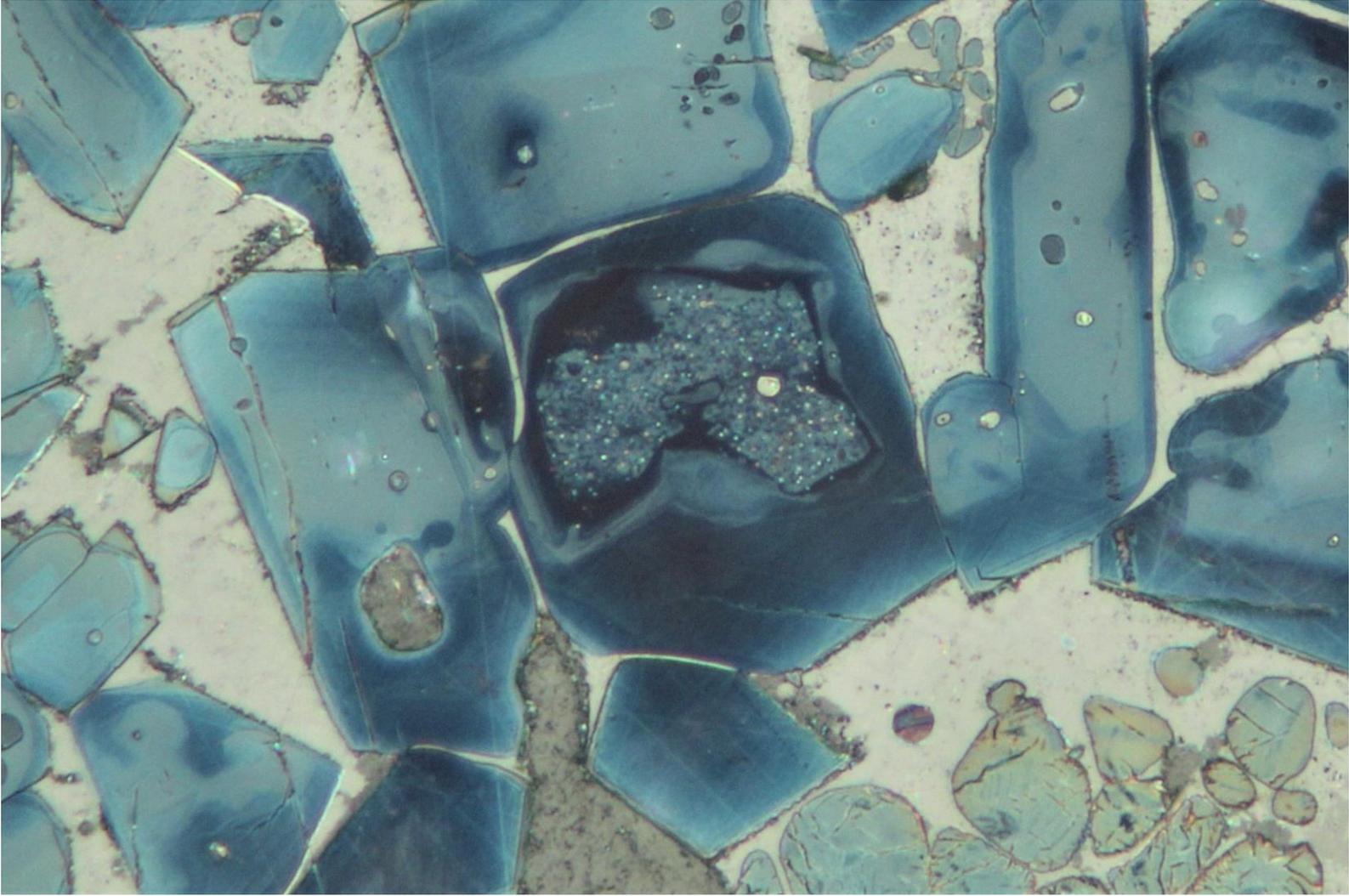
Large cluster of belite crystals due to coarse ash particles.



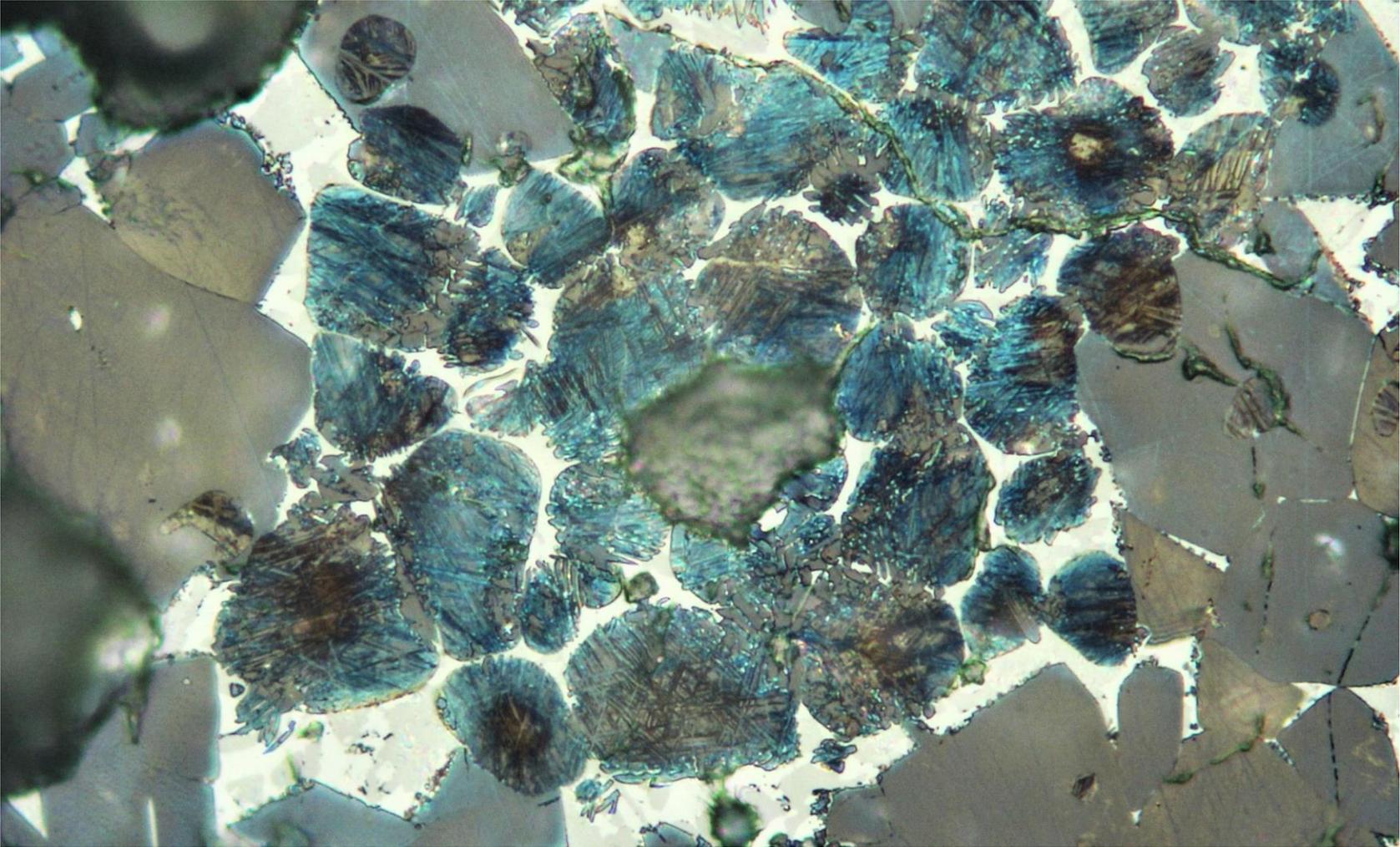
Secondary belite forming at the fringes of alite crystals due to slow cooling.



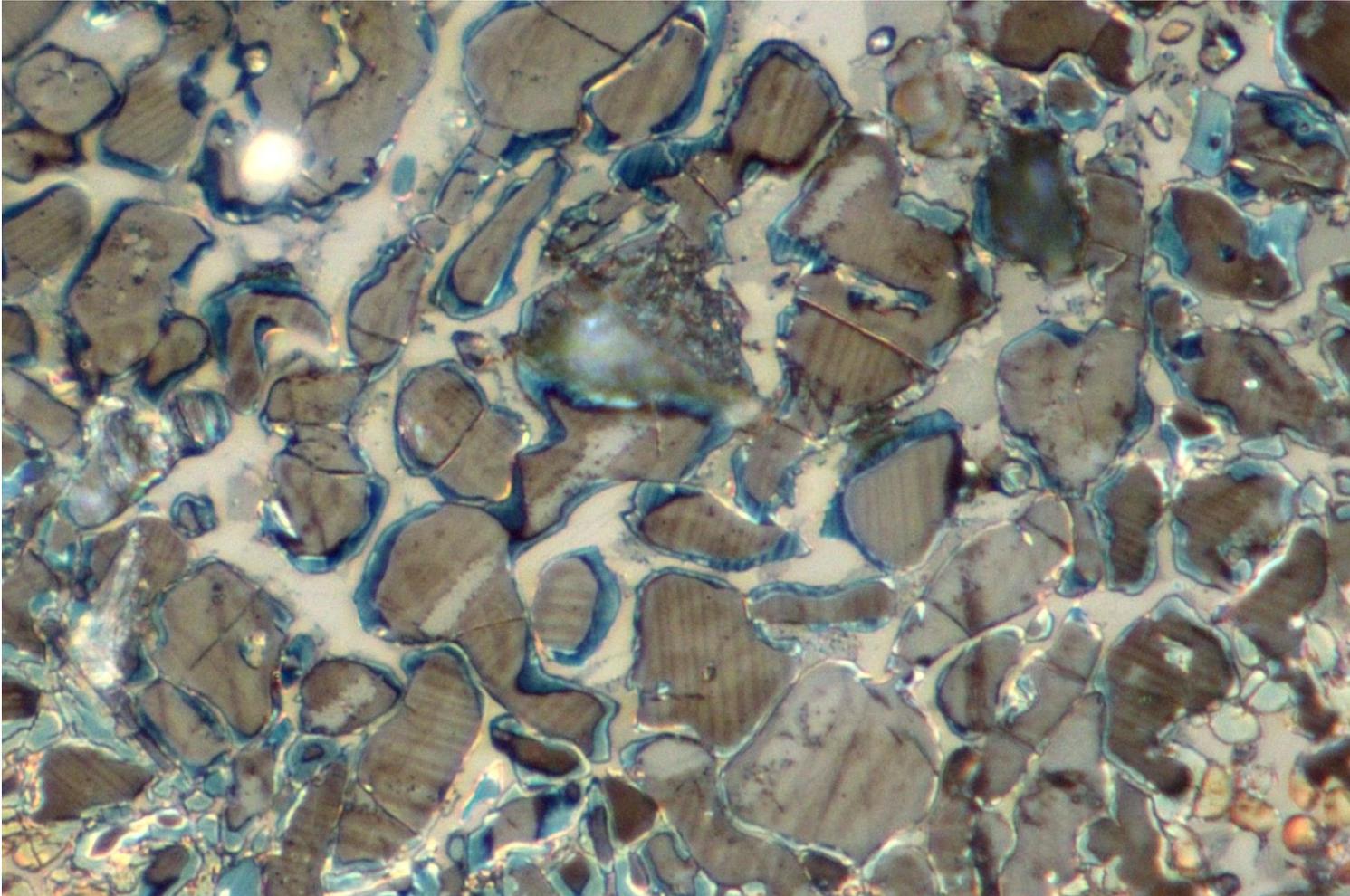
Zoning in alite crystals



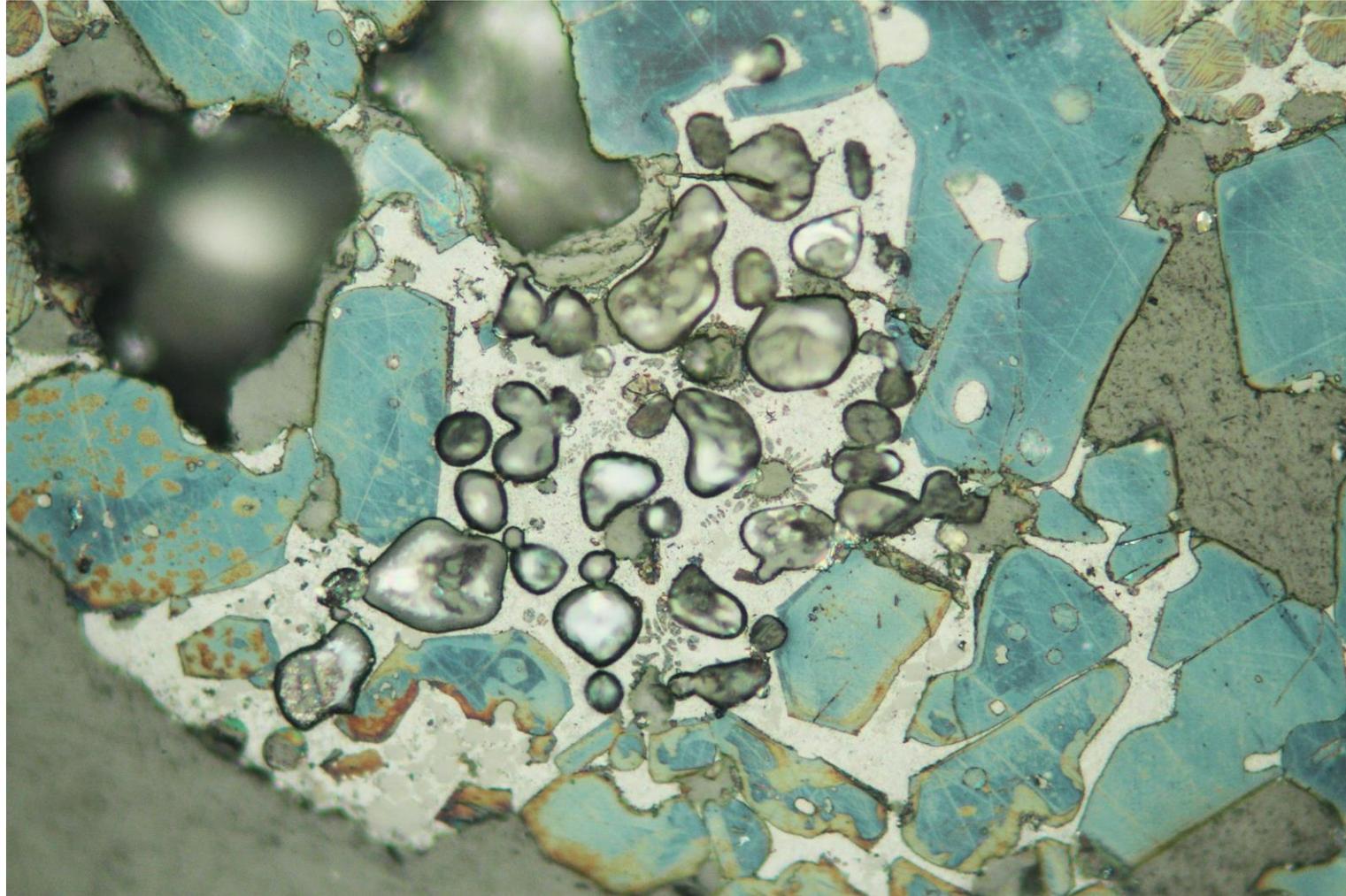
Slow cooling of belite crystals.



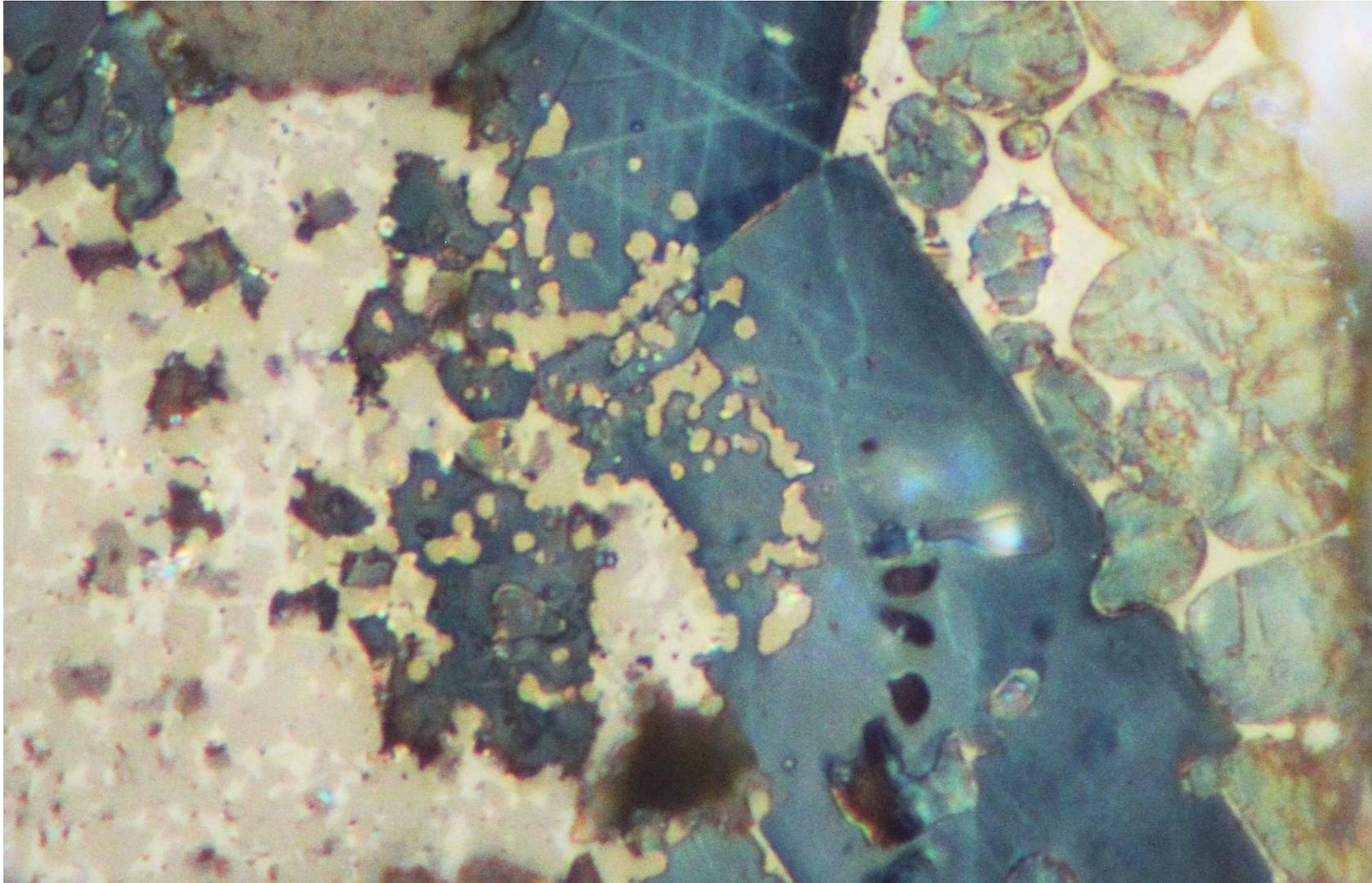
Secondary Type II belite crystals



Free lime cluster

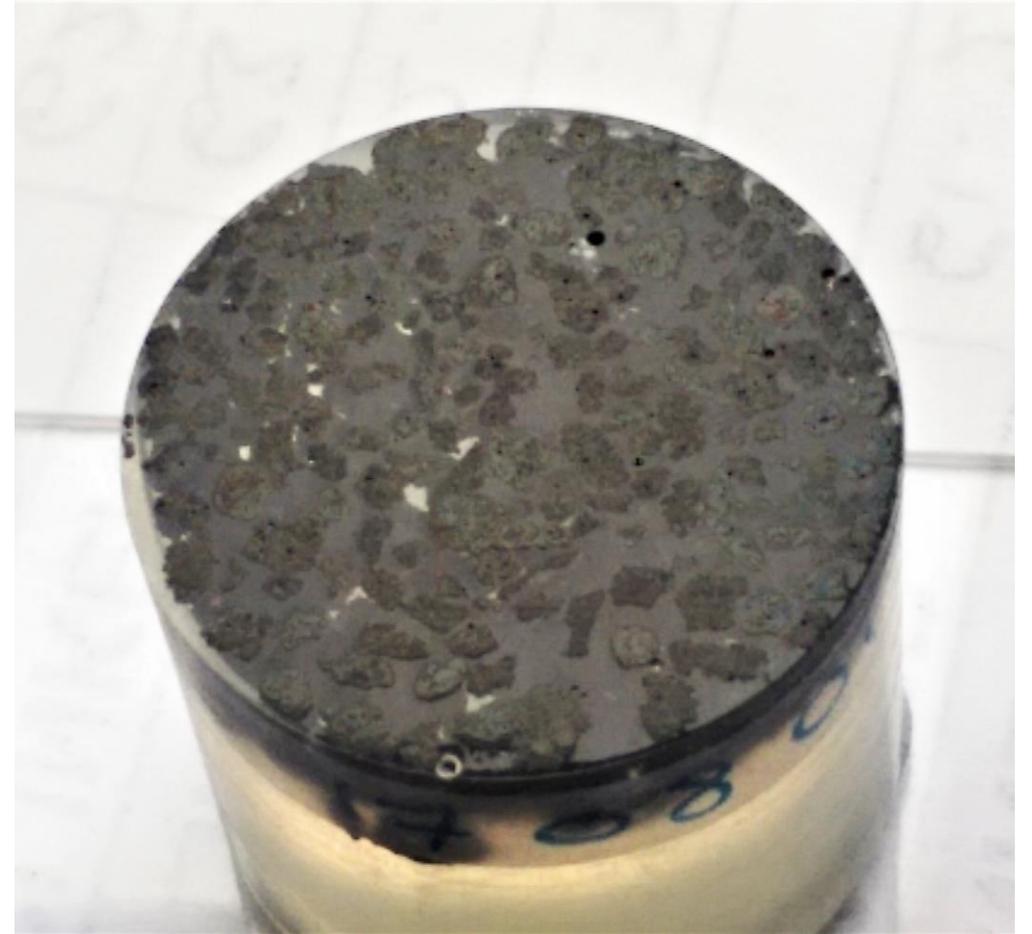


Periclase (MgO) affecting alite formation.



Sampling

- The polished section used during most clinker examinations contains of the order of 100 pieces of clinker which have been obtained by coning and quartering of the sample received from the cement factory then crushing to between 2mm and 5mm, then set in resin, cut and polished to produce the section.
- So, for a 2kg sample this ensures that a representative selection from the whole 2kg is examined.



Sampling

- Usually the most useful examinations are on grab samples taken at a time when the process details are known, then any changes in process can be related to changes in the clinker and in the long term changes in the clinker can be used to pinpoint unspotted variations in the process.

Examination Procedure

In my laboratory a standard examination comprises the following steps.

1. Point count of the main phases, alite, belite, matrix (essentially C_3A and C_4AF) and free lime.
2. Measurement of 100 randomly selected crystals of alite and 100 of belite.
3. Completion of sheet of observations
4. Photographs of main features
5. Report with comments of findings.

Point counting



In point counting, the polished section of clinker is placed on a specialist microscope stage which moves the specimen a predefined distance with a click of the mouse.

At each point the mineral beneath the cross hairs of the microscope is selected from a list, the mineral is recorded and the stage moves to the next point.

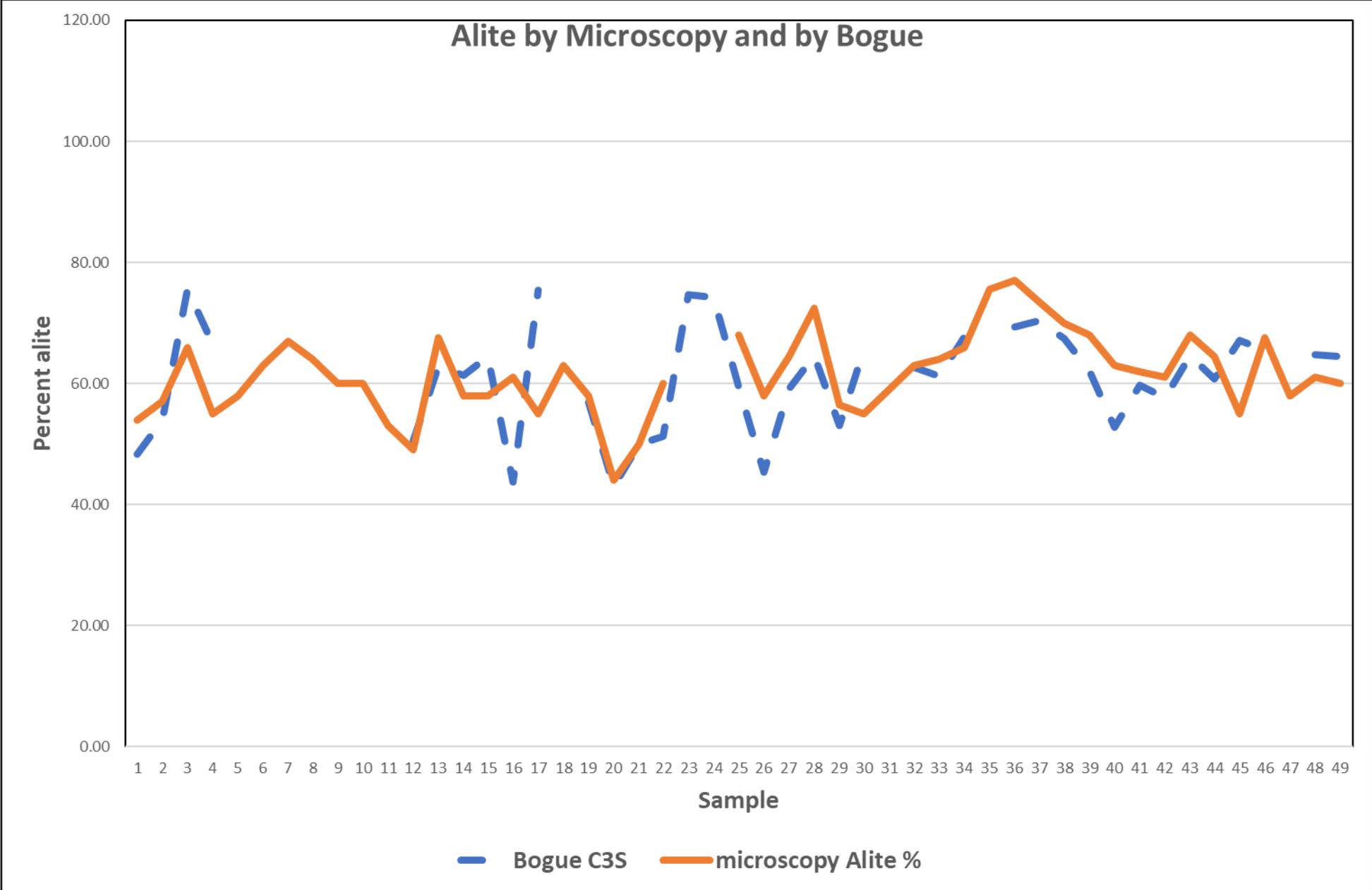
Point counting

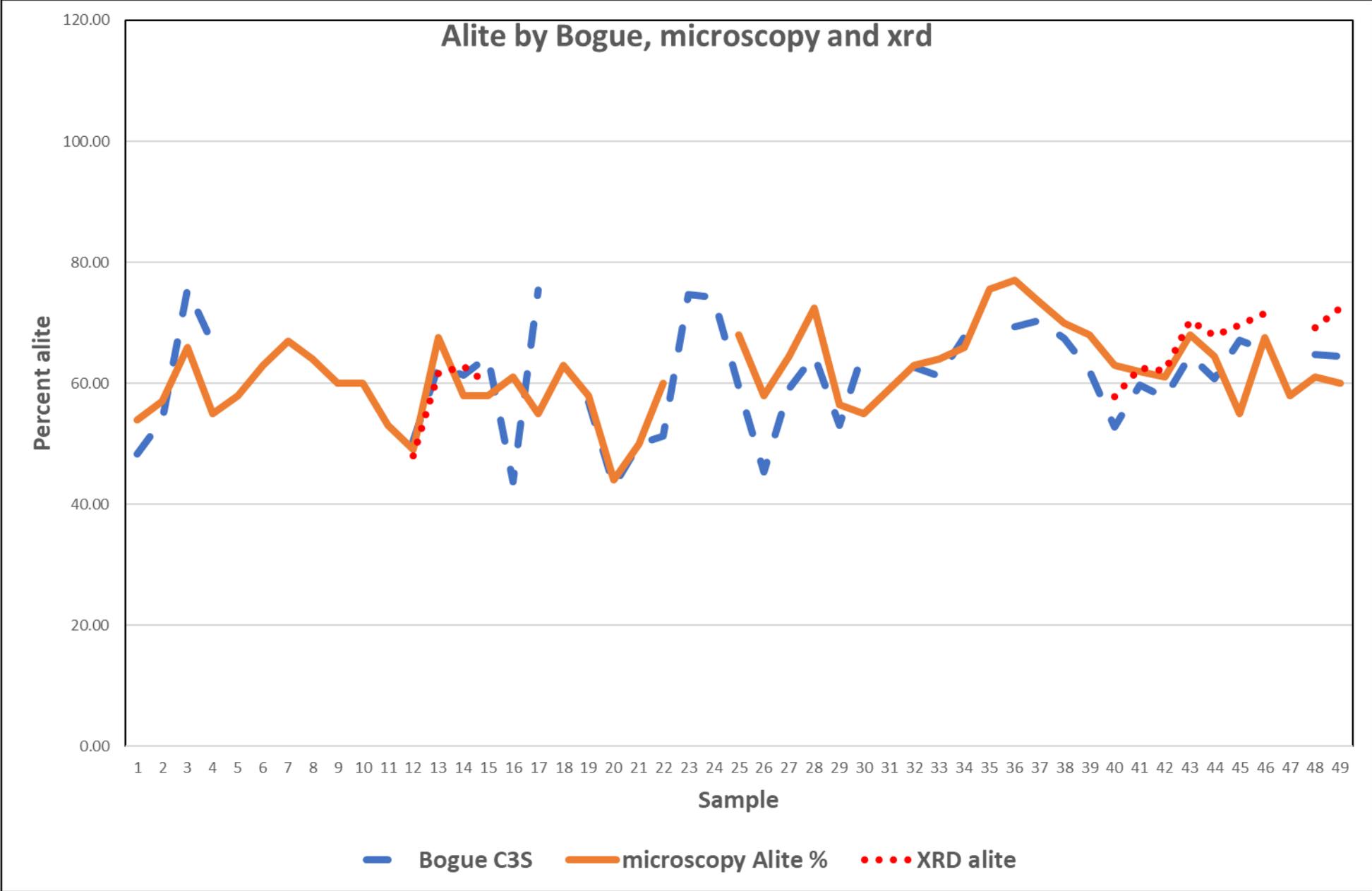
The number of points which need to be counted depends on the phase which is of most interest. In cement clinker the most important phase is the alite which is generally about 60% or higher. Some trials using the same clinker sample with different numbers of counts gave a difference of less than 3% alite using 100 counts or 1000 counts. For most samples I use 200 counts.

There is an ASTM for point counting clinker which gives a requirement of 3000 counts per sample. This would take several hours on a clinker polished section and is rarely justifiable. The reason for the high number is to ensure inclusion of phases such as alkali sulphates at levels of less than 1%. It seems probable that the chemical analysis will give a better idea with very much less time used.

Why point count?

- The Bogue calculation assumes that the alite, belite, ferrite and aluminate are the only phases present and they are all pure C_3S , C_2S , C_4AF and C_3A . While it gives a potential compound composition, in practice all these phases contain impurities which alter their proportions in the clinker.
- The difference in the quantity of alite measured by microscopy and that calculated using Bogue gives information on what may be happening. For example, if the burning zone is under severe reducing conditions the Fe_2O_3 reduces to FeO which can replace CaO in alite increasing its quantity. Some alite crystals also contain a large number of inclusions which also boost the quantity of alite present.

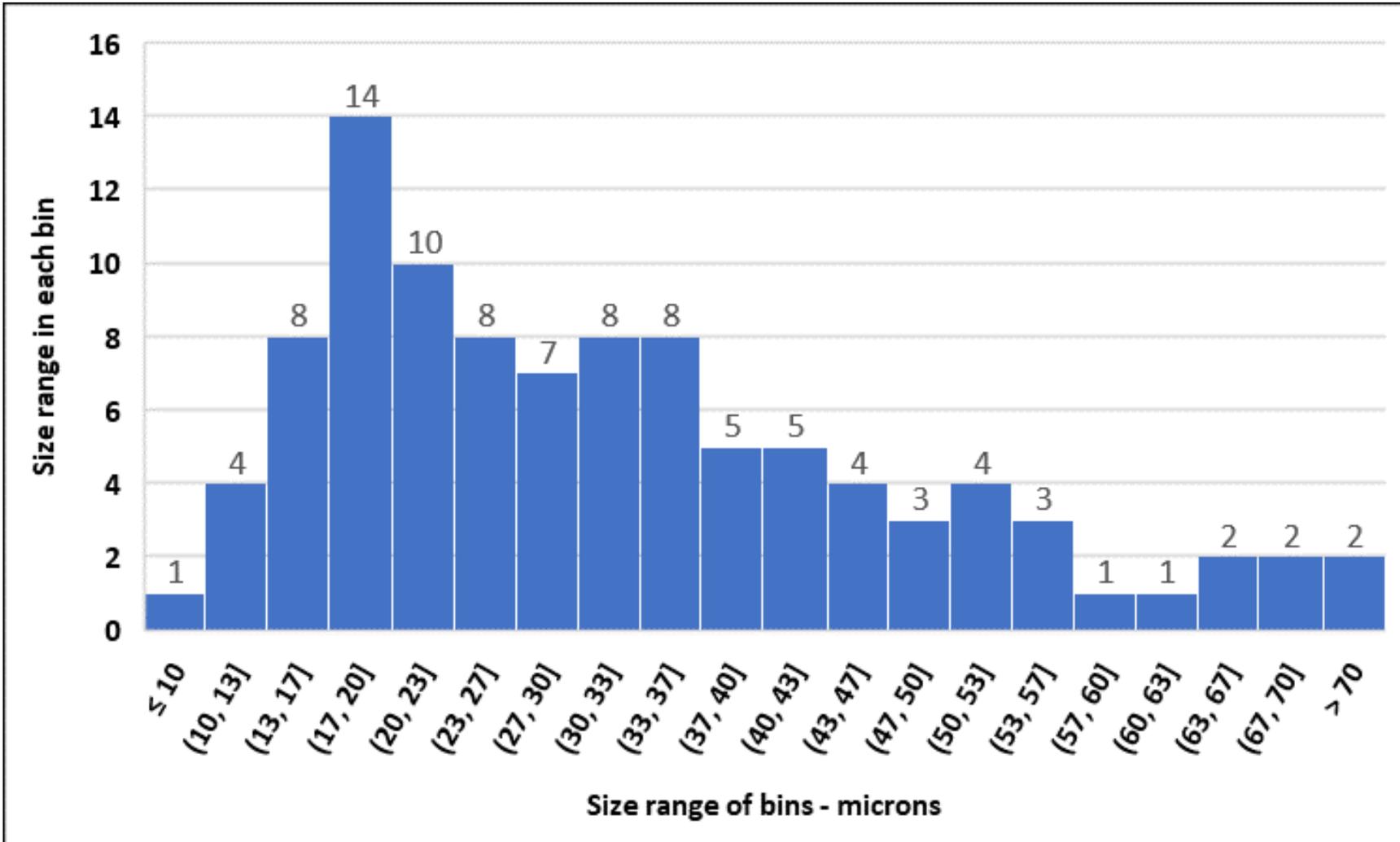




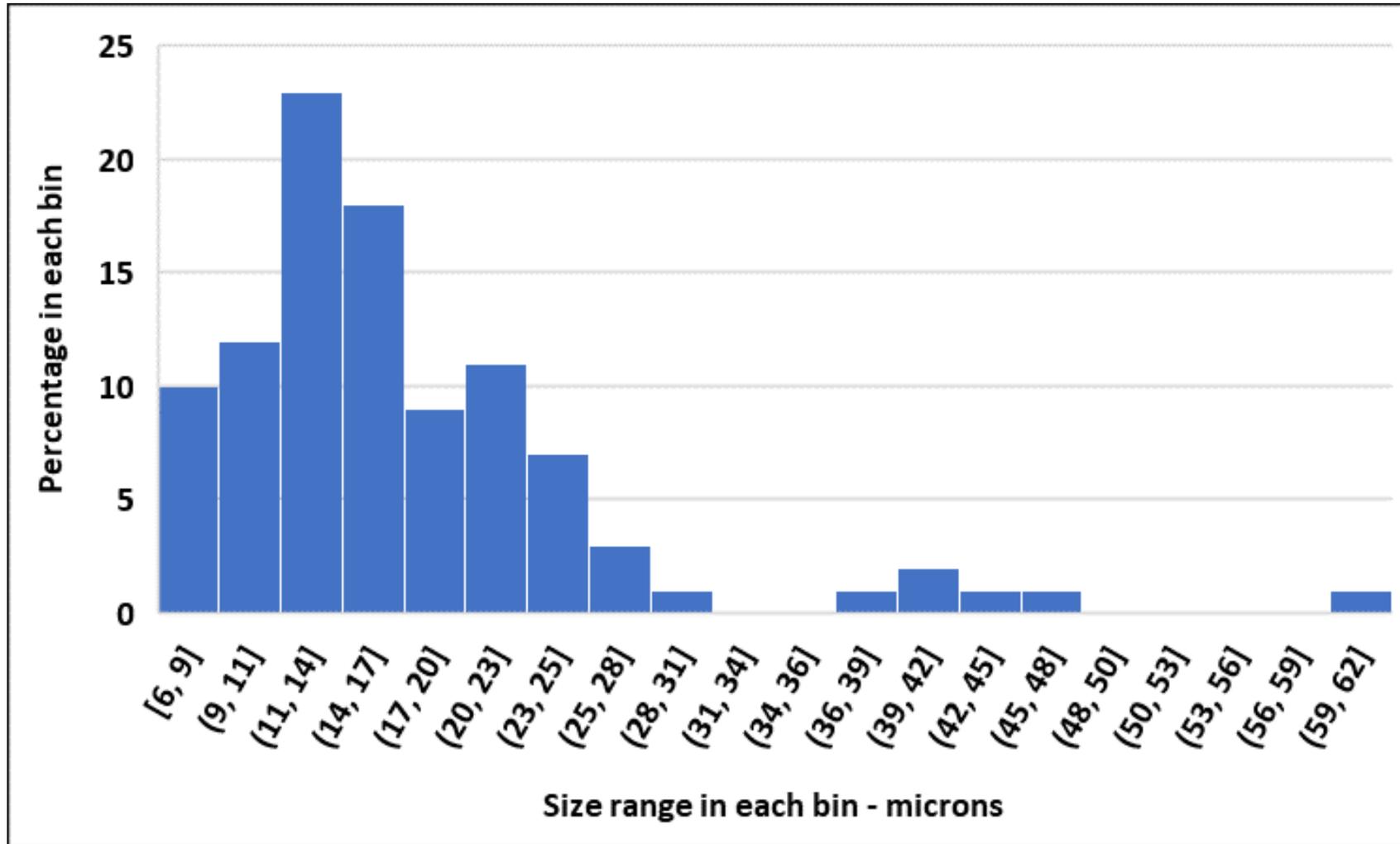
Crystal sizes

- From the Ono methodology the size of the alite and belite crystals were seen to be related to the quality of the cement. However, Ono measured just one group of crystals, those subjectively thought to be the most common size.
- Using the same mechanical stage as for the point counting it is now possible to use software to measure the crystal beneath the cross wire which will be recorded and moved on the next crystal. Some results of 100 randomly selected measurements from clinkers are shown on the next slides.

Crystal sizes - alite



Crystal sizes - belite

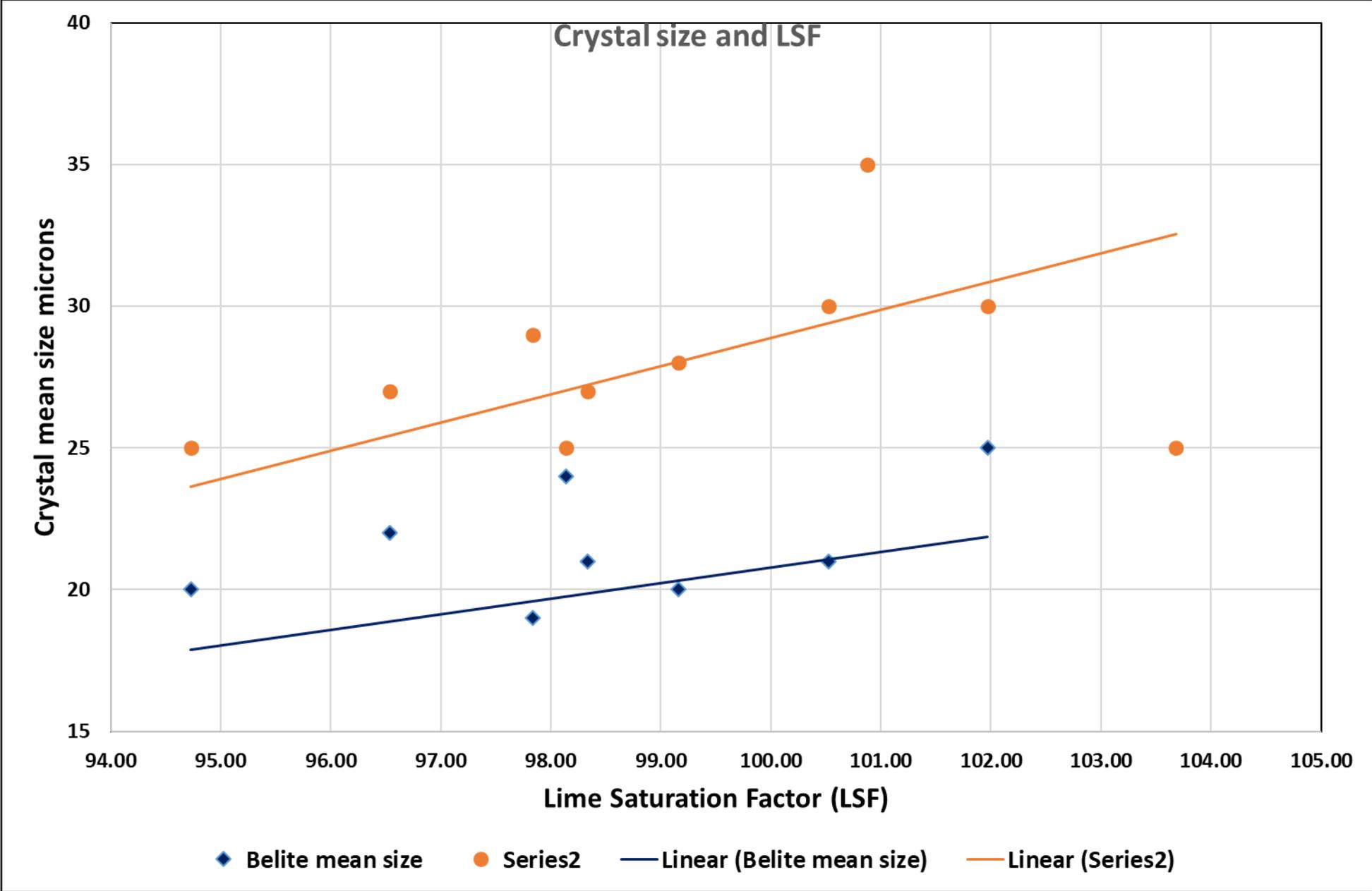


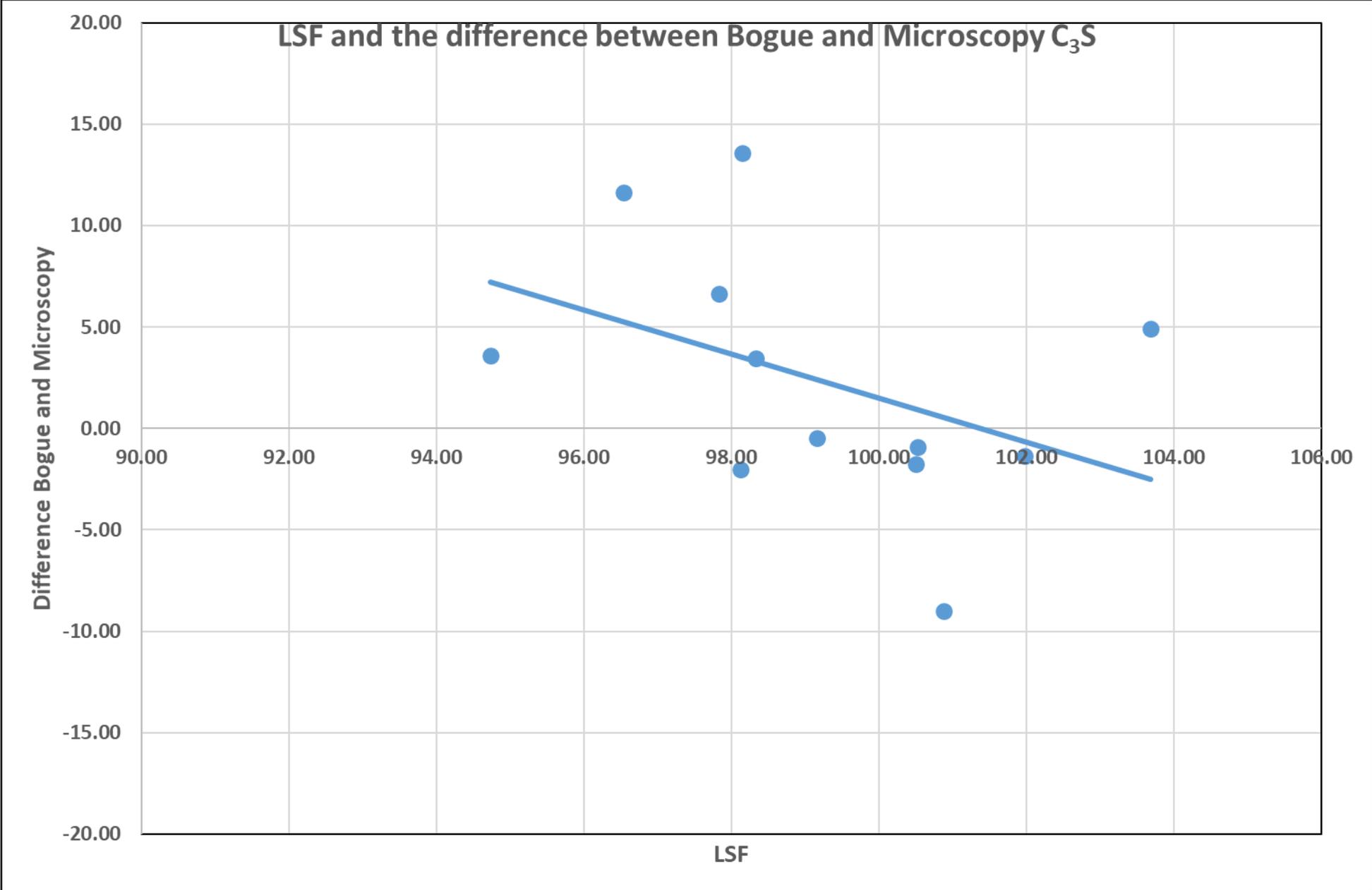
Observations.

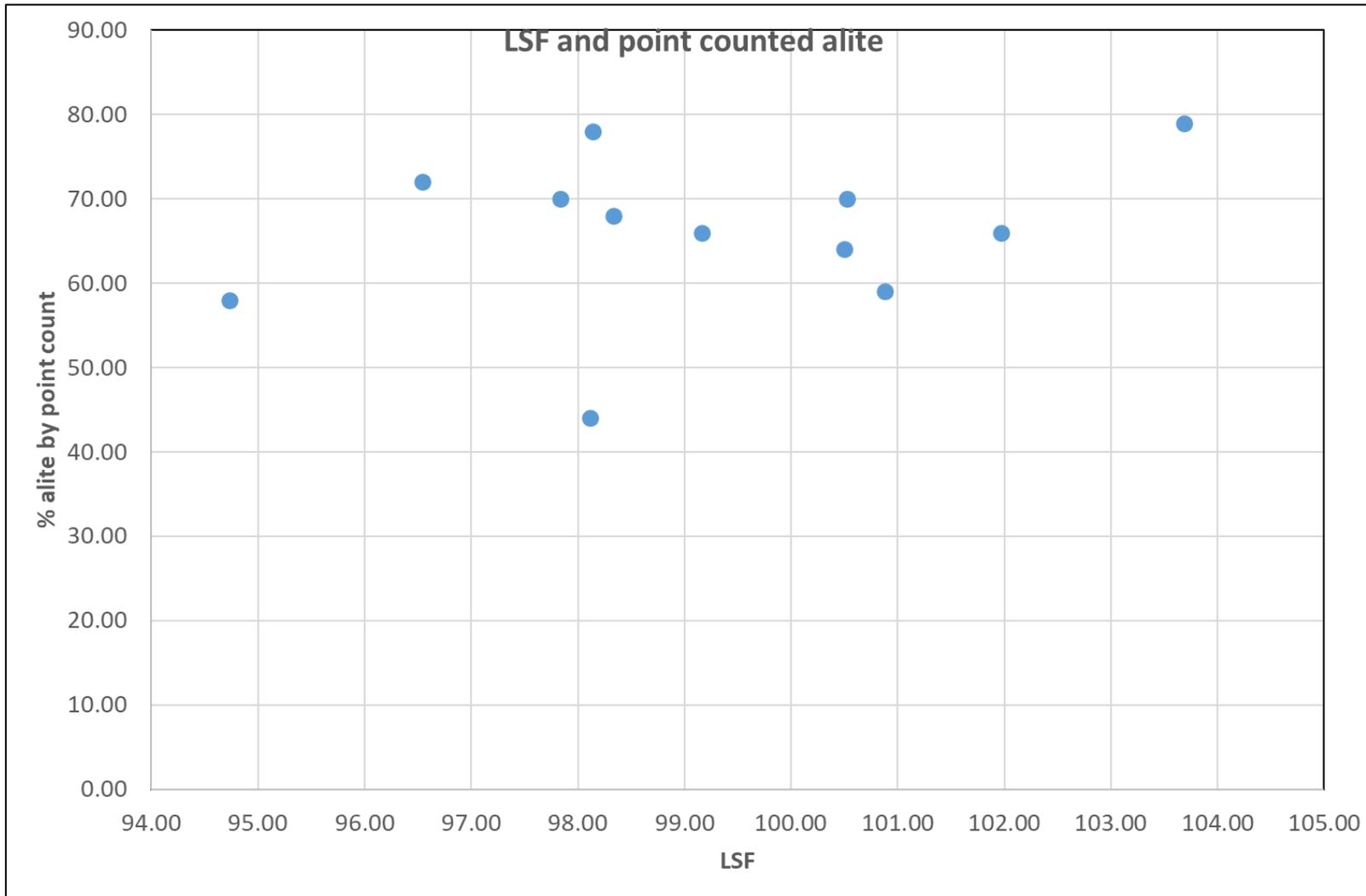
	Clinker
Alite average size (μ)	26
Alite max. size(μ)	90
Alite shape*	A - SA
Alite size sd	12
Zoned alite?	no
Alite main inclusions	Rare, mostly belite
Belite size mean (μ)	22
Belite max. size(μ)	100
Belite size sd	13
Belite Type (Insley)	Type I
Belite recrystallised	partly
Belite crystal extensions?	small
Belite clusters	
- coarse silica	yes
- ash	
- other	shale
Matrix size (μ)**	6
Cooling rate	Moderately slow
C ₄ AF or C ₃ A dominant?	Equal
C ₃ A prismatic?	Minor
Free lime mean cluster size(μ)	Generally 100-200 μ . Mixed with alite 700 μ
Free lime cluster shape	Round/angular
Alite degraded?	yes
Belite visible in matrix?	yes
Clinker reduced?	minor

Summary of Factory 1

- Changes in Lime Saturation Factor (LSF) had pronounced effects on the clinker.
 - Higher LSF produced larger crystals
 - Higher LSF gave a smaller difference between Bogue C_3S and microscopy alite
 - As a result – higher LSF did not necessarily give higher alite percentage





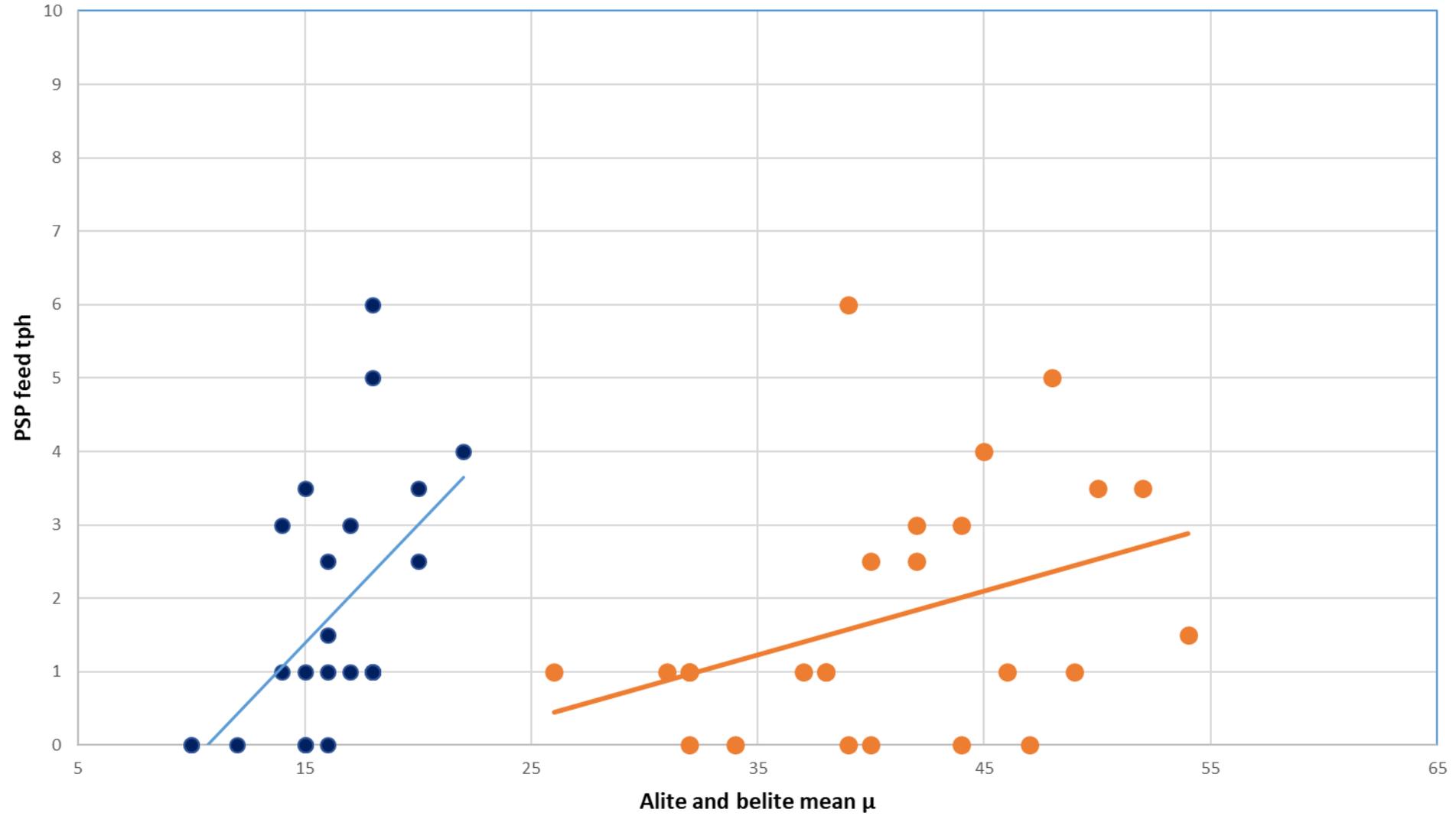


Increasing the LSF does not necessarily give an increase in alite percentage although the Bogue calculation would suggest that it would.

Summary of Factory 2

- Use of Processed Sewage Pellets (PSP) as fuel has an effect on the crystal sizes.
- Increase in use of shredded tyres as fuel produces a lower proportion of alite.

Alite and belite mean size/PSP tph



● Belite mean ● Alite mean — Linear (Belite mean) — Linear (Alite mean)

