

**Petrography and Characterization of Alteration in
Concrete Containing Aggregates from the
Umbria Marche Sequence, Italy**

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Abstract

Petrographic examination and microprobe analysis was performed on concrete cores of different ages containing aggregates derived from the Umbria-Marche stratigraphic sequence of Italy. The study's aim was to evaluate the performance of Umbria-Marche carbonate and chert aggregate over time and to determine causes of deterioration in older samples. Thin sections were examined for the development of reaction products, microcracking and reaction rims. Cores ranged in age from 4 to 43 years and revealed no clear progression of deleterious chemical or mechanical reactions. Cement contained no potassium, sodium or sulfur, eliminating the possibility of several deleterious chemical processes. Due to high natural pozzolan content, none of the samples contained portlandite. Visible discoloration rims on both chert and limestone clasts in the aggregate were present prior to emplacement in cement and are likely caused by density variations relating to hydration. The majority of fractures observed in thin section occurred during thin section preparation, and there is evidence that fractures in chert aggregate present prior to sampling did not occur *in situ* in the concrete. Alteration related to sampling and analytical methods is discussed and a physical mechanism is postulated as the cause for the deterioration of a concrete produced in 1961.

Keywords: Umbria-Marche, Italy, concrete, cement, aggregate, fractures

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Introduction

Concrete is a man made conglomerate material consisting of particles, or aggregate, in a fine cement matrix. The composition of aggregates influences the long-term behavior of the concrete, as delayed reactions occurring between the cement and aggregate can cause fracturing and structural weakening. The concrete industry screens the reactivity potential of aggregates in a variety of ways (Stokowski and Dickerson, 1987). Popular methods include, but are not limited to, petrographic analysis and immersion in chemical solution for periods up to and exceeding a month. Petrographic analysis reveals the presence of minerals with known adverse effects on the setting and long term performance of the concrete, while immersion quantifies the severity of reactivity in terms of percent expansion volume. These laboratory practices are conducted before the aggregate is introduced into general use. There is currently no published evaluation of the Umbria Marche sequence as an aggregate source using the methods outlined above or otherwise. Concrete structures built over a 40 year span in Coldigioco, Italy present the petrographer an opportunity to evaluate the performance of aggregates derived from the Umbria-Marche stratigraphic sequence as they behave *in situ*. The record presented by the aging concrete samples should reveal the long term adverse effects of reactive components in the sequence that would cause premature deterioration. Coldigioco concretes are made with the same cement type, eliminating large variations in cement composition as a factor for variation in behavior over time. It should be noted that while the concretes do not significantly vary compositionally, there are proportional differences, described by Montanari (2004):

“The proportions of water, cement, and aggregate are usually 2 buckets (about 20 liter) of water per 50 kg 3.25 Portland cement per 200-250 kg of aggregate,

everything carefully dosed... by eye. So, you may find different concretes even in things that have been manufactured by the same mason, in the same day, depending on whether he did the job before or after lunch, and on how much wine he drank (and also on the type of wine).”

Geologic background: The Umbria Marche Sequence

Concrete aggregates from the Umbria-Marche originate directly as talus slopes or indirectly as river terrace deposits. The sequence is primarily limestone containing calcified foraminifera and calcite veins with interbedded chert and marl layers (Figure 1) (Montanari et al., 2002). Localized dolomitization takes place in some areas but is minimal and not significant with regard to the bulk of the formation (Montanari, 2004).

Cement Constituents

Chemical constituents of cement affect the mineralogy and composition of the crystalline and amorphous phases that develop during curing. Portland cement is a lump term encompassing cements composed primarily of ‘clinker’ a product made by heating limestone and clay aluminosilicates to 1500 degrees C to drive off CO₂ (St John et al., 1998). The result is a product composed primarily of calcium silicates in the form C₂S and C₃S¹. CaO is also present. The principal constituents of typical cement clinker are outlined in Table 1.

Table 1: Common Phases in Cement	
Clinker Phases (shorthand notation)	
Alite/ tricalcium silicate	C ₃ S
Belite/ dicalcium silicate	C ₂ S
Tricalcium aluminate	C ₃ A
Ferrite	C ₄ AF
Free Lime	CaO
Cement Hydrates	
Ettringite/ calcium sulfoaluminate hydrate	3CaO.Al ₂ O ₃ .3CaSO ₄ .32H ₂ O
Portlandite/ calcium hydroxide	Ca(OH) ₂
Limonite/ iron oxide hydrate	Fe ₂ O ₃ . nH ₂ O
Calcium silicate hydrate (C-S-H)	(CaO) _n (.SiO ₂) _n . nH ₂ O
Alkali-silica gel	Na ₂ O.K ₂ O.CaO.SiO ₂ . nH ₂ O

Cement hydration products

When hydrated, the calcium silicates form a non-ideal binary solid solution series with endmembers $\text{Ca}(\text{OH})_2(\text{s})$ and $\text{CaH}_2\text{SiO}_4(\text{s})$ (Börjesson et al., 1997). These calcium silicate hydrates typically make up 70% of ordinary portland cement, with 20% portlandite produced from the hydration of excess CaO that has not been consumed by reactive silica (St John et al., 1998). Birchall (1978) presents a schematic representation of clinker hydration (Figure 2) and Double's (1978) early investigation of mechanisms of hydration includes scanning electron micrographs of products (Figure 3). Gypsum is commonly added as a set retardant and supplies the sulfur necessary for the formation of ettringite (St John et al., 1998).

Pozzolan and the pozzolanic reaction

Coldigioco concretes contain Type IV Portland cement², also known as pozzolanic cement. Pozzolanic cements are a subset of the Portland family containing pozzolan, a reactive glassy inclusion. In the pozzolanic reaction portlandite and reactive siliceous sources produce additional calcium silicate hydrates (Moropoulou et al., 2004). Pozzolanic cements are identified in part based on the absence of portlandite, which is entirely consumed in the pozzolanic reaction (St. John et al., 1998). Synthetic pozzolan consists of spheroid particles called fly ash, a byproduct of coal combustion. Natural pozzolans include diatomite, pumicite and tuff and in Italy are primarily the volcanic ashes abundant in the volcanic deposits of northern Italy (Montanari, 2004).

² Concrete made in 2000 is known to have been mixed using this type of cement. All prior concretes utilized the same supplier and was specified for the same purpose and are assumed to have been consistent.

Alteration Reactions

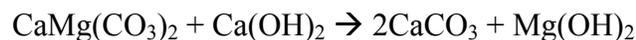
Delayed formation of expansive products or shrinking of existing hydration products characterizes damaging alteration reactions in concrete. The most common of these reactions are the following:

Alkali-silicate reaction (ASR)

Unstable silicates react with hydroxyl ions and sodium and potassium in several steps to form an amorphous hydrate called alkali-silica gel (Figure 4). Humidity in the cement causes ASR products to swell and produce fracturing (Martindale et al., 2001; Mather, 1999). In cements with low alkali content ASR potential is minimal; reactive silica aggregates may be used in cement containing less than 0.60% alkalis calculated as sodium oxide equivalent ($\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$) (Mather, 1999). ASR may also be mitigated by pozzolan addition, as the silica in pozzolan consumes $\text{Ca}(\text{OH})_2$ to form additional calcium silicate hydrates, making it unavailable for ASR product formation (St. John, 1998). Alkali silica reaction is extremely common in high alkali cements but can also occur in low alkali cements where alkalis are introduced into the system by de-icing salts and groundwater.

Dedolomitization

Alkali-carbonate reactions are benign for the most part, resulting in no significant change in volume. Dedolomitization, however, creates brucite and calcite, whose volume exceeds that of the reactants:



Dolomitic aggregates undergoing this process will have calcium enriched rims and have a loose bond with the surrounding paste (Willingham et al.).

Sulfate attack

Sulfate attacks concrete in a variety of ways resulting in the formation of gypsum, ettringite or brucite, all of which cause expansion and cracking. Sulfate attack also dissolves existing cement hydration products, weakening the concrete. Calcium aluminate hydrates in cement react with gypsum to form ettringite. Other sulfates in solution will react with calcium hydroxide to form gypsum, which in turn will form ettringite as described (St. John, 1998). Magnesium sulfate reacts with calcium silicate hydrates to form both gypsum and brucite.

Methods

Sample Collection

Vertical cores 2.5 cm in diameter and up to 7.5 cm in length were taken with a water-cooled diamond bit drill for seven concrete structures in Coldigioco, Italy (Figure 5). Sample sites were selected based on uniformity of exposure to weathering; all structures were ground level foundations or containment walls. None of the structures were subject to external compressive and/or tensional forces. Two cores were taken for each of the seven structures. The dates of each structure's production are: 1961, 1970, 1988, 1992, 1994, and 2000³. No significant deterioration was visible except in the 1961 sample, which was crumbling, and an additional structure of unknown age, labeled as sample 19--.

³ Ages according to Coldigioco resident Alessandro Montanari.

Thin section preparation

One core from each structure was sent to Spectrum Petrographics for thin section preparation. Two thin sections were created for each core: one large scale size made along the central vertical axis and one standard size along the horizontal axis at a depth of 8mm, the shallowest depth at which all of the cores were uniformly intact⁴. The thin sections were polished down to 2 microns for microprobe analysis.

Three different samples of loose aggregate were taken from sources in the Marche region: a river terrace deposit from an aggregate collection site in Jesi, talus from a slope near Monte San Vicino and crushed wet-seived talus from an aggregate distributor in Cingoli. The loose aggregate samples were emplaced in Hillquist epoxy and vacuum desiccated for thin section preparation and polished down to 15 microns.

A thin section was produced from the 1961 core using red dye impregnated epoxy to mount the sample to the glass slide. The dyed epoxy filled existing fractures in the sample, enabling distinction between pre-existing fractures and those produced during thin section preparation.

Silicate content of the aggregates

Approximately 750g of each aggregate sample was dried overnight in an oven at 90 C and weighed. 37% HCl was added to each sample in 100ml increments until all carbonate dissolved. The remaining fraction was rinsed, dried and weighed.

Petrographic analysis

An Olympus BXS1 microscope outfitted with a Nikon DXM1200 camera was used for petrography and photomicrographs.

⁴ Some cores experienced surficial damage during sample collection.

Microprobe Analysis

Microprobe analysis was conducted at the University of Minnesota Electron Microprobe facility with the assistance of Laboratory Supervisor Ellery Frahm. Semi quantitative major oxide data was collected using wavelength dispersal spectrometry (WDS). WDS disperses x rays by wavelength rather than energy, creating a unique wavelength profile when outer shell electrons replace inner shell electrons removed by the microprobe electron beam for each oxide selected. Oxides selected included MgO, CaO, K₂O, Na₂O, SO₄, SiO₂, Al₂O₃ and FeO. Spot, line and map analyses were conducted on samples 2000 and 19--. Backscattered electron micrographs were taken.

Results

Aggregate

The Jesi aggregate, derived from a local river terrace deposit, consists of sub-to-well rounded fossiliferous limestone clasts containing calcite veins and calcified foraminifera. Clasts have discolored rims of light, dark or both light and dark bands (Figure 6). Chert makes up approximately 18% of the aggregate by weight, with particles ranging from angular to subrounded. On average, chert particles are smaller than the carbonate clasts. The majority of chert particles have light outer rims with a brown interior (Figure 7). Some fractures within the particles also have lightened edges.

The Cingoli aggregate has the same properties of the Jesi sample, with the exception that limestone clasts are smaller and chert accounts for approximately 5% of total sample weight.

The Monte San Vicino aggregate contains angular limestone and chert clasts lacking uniform discolored rims in both. Chert particles, 12% of total sample weight, have splotchy, uneven brown discoloration. Chert particles in all samples displayed abundant fracturing (Figure 8).

Electron microprobe line tests on apparent reaction rims in the aggregate did not reveal significant compositional variation. A line test along a carbonate rim showed no significant variation in Mg, Na, or Ca, elements chosen as indicators of dedolomitization (Figures 9.1 and 9.2). Line tests across a fracture in a chert clast showed no compositional variation correlating to discoloration (Figures 10.1 and 10.2).

Cement

The cement matrix contained from 2 to 20% undulatory quartz grains and from 5 to 30% pozzolanic additive. Few unhydrated grains of clinker remained (>.5%) suggesting a water/cement ratio of .6 or more, making quantification of other additions infeasible (French 1991). No ettringite or portlandite was observed in thin section or sample cores. The remainder of matrix material was amorphous calcium silicate hydrate. All samples contained some degree of map cracking in the cement matrix, with cracks both propagating into aggregates and following the aggregate-matrix interface (Figure 11). No significant differences in fracturing could be seen through the depth of an individual sample or between differently aged samples.

Semi-quantitative broad and focused electron microprobe spot tests of the cement matrix revealed a standard composition of 35% SiO₂, 55% CaO, 10% Al₂O₃ with less than 1% K₂O.⁵ No other elements contributed significantly to the cement composition. Focused spot analysis of microcrystalline matrix material showed crystals containing up

⁵ Figures contain one percent error.

to 23% Al₂O₃, but the majority of crystals had broadly fluctuating SiO₂ and CaO contents, with Al₂O₃ ranging from 4 to 12%.

Discussion

Sampling Alteration in Concrete

Techniques used in thin section preparation often alter the sample to create new features that can be indistinguishable from existing features. It is with great difficulty that these secondary features are resolved from characteristics of the unaltered sample, and often petrographers incorrectly infer the presence of deleterious reactions not present in a sample (Sturm, 2004).

Grinding debris inclusion (Figure 12)

Vesicles of entrained air in the cement become filled with grinding debris. The debris may collect around the vesicle edge or fill it completely, while other vesicles remain unaltered. Fracturing observed in the aggregate and cement around such fillings occurs when the sample, wetted from grinding, dries and desiccates. The fillings are qualitatively similar to alkali silica gel deposits and have previously been identified as such (Montanari, 2004; Sturm, 2004). Apparent porosity is reduced in such samples, and deterioration caused by porosity may not be correctly identified in such samples.

Mechanical stress fracturing

Sampling with coring devices exerts considerable stress on cement and may result in fracturing. Dull blades and coarse grinding media used in thin section preparation will fracture brittle inclusions in the concrete (Figure 7). These fractures often extend into the matrix. Existing fractures may propagate further within the clast and into the cement

matrix. Fractures with alteration such as interstitial crystal growth or discoloration can be assumed as present prior to thin section preparation.

Dessication cracking

A sample with hydrous phases will contract and crack when heated for drying or epoxy dispersion. Continual wetting and drying of the sample promotes map-cracking as the sample expands and contracts. Changes in the internal humidity of a sample occur slowly *in situ* and the rapid, drastic changes in humidity that occur during traditional thin section preparation put the sample under undue stress.

Ammouche et al. (2000) proposed a method for identifying pre-existing microcracks in concrete samples. If a sample is impregnated with a low viscosity epoxy containing a marker dye prior to cutting, grinding and exposure to heat it is possible to distinguish between existing fractures and those caused post-sampling. Existing fractures will contain the dye marker, though fractures created during coring will also be filled. Results from this technique were ambiguous as distinction could not be made between fractures created by the preparation of surfaces created for dye impregnation and fractures present prior to sampling.

Cement chemistry implications

The absence of potassium, sodium and sulfur as determined by microprobe analysis of cement and aggregates eliminates alkali-silica and sulfate reactions as mechanisms of microcracking in the samples. Common hydration products such as portlandite and ettringite were not observed in thin section. Ettringite requires sulfur introduced from clinker or gypsum to form and so is not present in the samples. Depletion of portlandite is characteristic of pozzolanic cements; ordinary portland cement

yields 20% portlandite upon hydration (Diamond, 1976). Portlandite appears to have been completely consumed by pozzolan additions and converted to calcium silicate hydrate, evidenced by the fact that unreacted pozzolan is visible in the matrix and is therefore in excess. The difficulty of determining aluminate and ferrite compositions using microprobe analysis has been documented by Kristmann (1978) and, accordingly, results regarding these phases are ambiguous.

Apparent aggregate alteration

Insufficient magnesium was found in the carbonate clasts for dedolomitization to occur. Rims visible on both limestone and chert clasts do not reflect compositional variation in any of the most abundant elements in the system, but changes in density. The majority of rounded riverbed clasts display these rims while talus material does not, suggesting the rims form during weathering and deposition. The probe damage observed on a chert clast is indicative of volatile phases such as water, suggesting that the rims around chert clasts can be attributed to hydration. Hydrolysis dictates fracture formation to some degree; three membered silica rings in amorphous silica are more easily hydrolyzed than four and five membered rings, so that the distribution and hydrolysis of three membered rings controls the distribution of fracture formation (West and Hench). Once fractures form fluid circulates easily within them and hydration occurs along the existing fracture paths. Rims on limestone aggregates did not display probe scarring, but that does not eliminate the possibility of a similar mechanism for their formation.

Fracturing in healthy and deteriorated samples

Petrographic analysis of bulk aggregate revealed pattern cracking in chert clasts. While the majority of these fractures occur during thin section preparation, those

exhibiting hydration along the fracture rim could have been present prior to emplacement in cement or occurred within the cement. Cracks propagating into the cement matrix from these altered fractures could have been caused as cracks widened as a consequence of thin section preparation or in *in situ*. Crystallization of minerals in the aluminosilicate solid solution series occurred along some fractures as pore solution precipitated out, indicating that these fractures existed in the concrete prior to sampling.

Similar cracking patterns were observed in healthy, intact concrete samples and the deteriorated 1961 sample. The similarity in thin section of two very different samples suggests that there is a low correlation between severity of microcracking in thin section and outward appearance of concrete. This is true for alkali aggregate reaction, where the degree of external cracking does not correlate well with the severity of the reaction internally (St. John, 1998). Another possibility is that damage to the sample incurred by thin section preparation resembles damage occurring to the sample *in situ*. Excessive microcracking caused by thin section preparation would then obscure genuine progression and propagation of microcracking over time. The latter appears more plausible in this case.

Freeze-thaw implications

For cements with a high proportion of natural pozzolan additions, an increase in water content increases porosity of the matrix, promoting fracture propagation (Berger et al., 1973). Colak (2003) found that resistance to freeze thaw deterioration decreased in cement with 20 to 30% pozzolan addition. Cements with 40% pozzolan replacement lost 20% of their original compressive strength after 60 freeze-thaw cycles.

According to the National Climatic Data Center, in the Marche region average relative humidity is 74% with an average temperature of 7 degrees C for months during which freezing occurs (2004). Wet weather, combined with mild winters hovering near the freezing point equates to many freeze-thaw cycles within a single winter having an effect on concrete.

Conclusion

The Coldigioco samples are primarily “healthy” concretes containing silicate aggregates emplaced in a low alkali, low sulfate cement matrix containing natural pozzolan additions. The composition of the cement is advantageous given the reactivity potential of the amorphous silica clasts, and insufficient alkalis and hydroxyl groups are available for alkali silica reaction to occur. Concordantly, high alkali cements should be avoided with Umbria Marche aggregates due to chert content. Dedolimitization is not a risk with this aggregate, as dolomitization occurs infrequently in the aggregate source. Fractures observed in chert are present prior to use as aggregate and may have expanded further once emplaced in cement due to hydration and freeze-thaw, propagating fractures into the cement matrix. This is the proposed mechanism for deterioration of the 1961 sample, as possible chemical mechanisms have been eliminated. The chemical stability afforded by pozzolan addition is gained at a mechanical cost, as these samples are less resistant to freeze thaw damage due to density loss and increased porosity.

Acknowledgements

I would like to thank Alessandro Montanari of the Osservatorio Geologico di Coldigioco for introducing me to the field of concrete petrography, and Dave Bice for helping me to develop this project. Ellery Frahm at the University of Minnesota Electron Microprobe facility provided his expertise, as well as Ronald Sturm of Construction Technology Laboratories. Last but not least, Mr. Tim Vick, my co-pilot.

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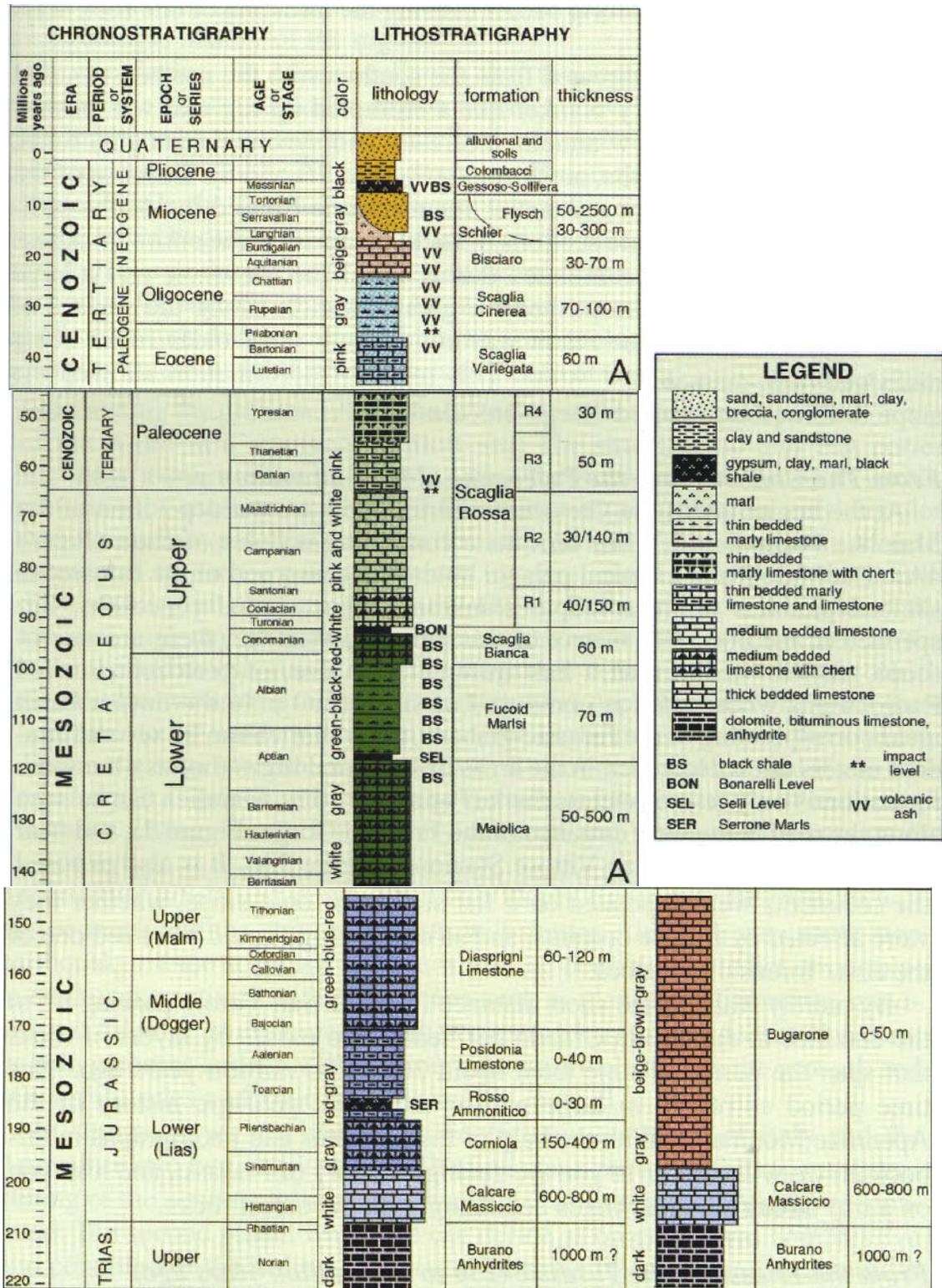


Figure 1: Stratigraphy of the Umbria-Marche sequence adapted from Montanari et al., 2002.

On the hydration of Portland cement

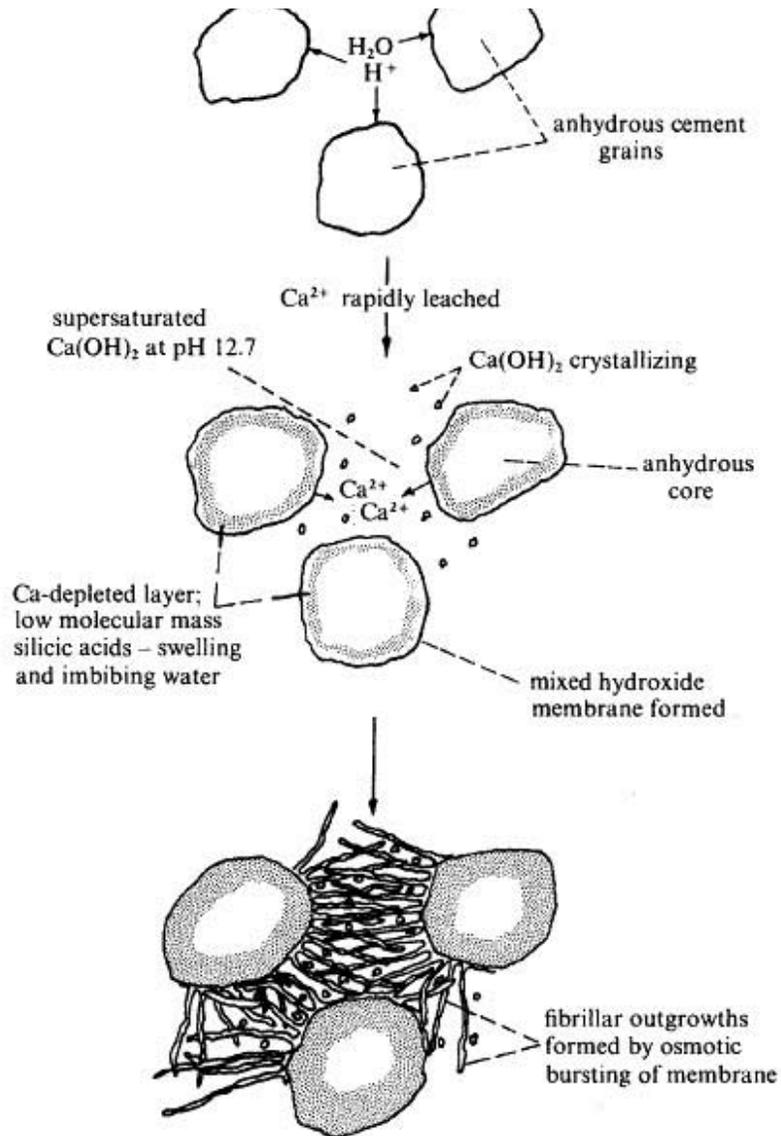


Figure 2: Hydration and setting of Portland cement. From Birchall et al, 1978.

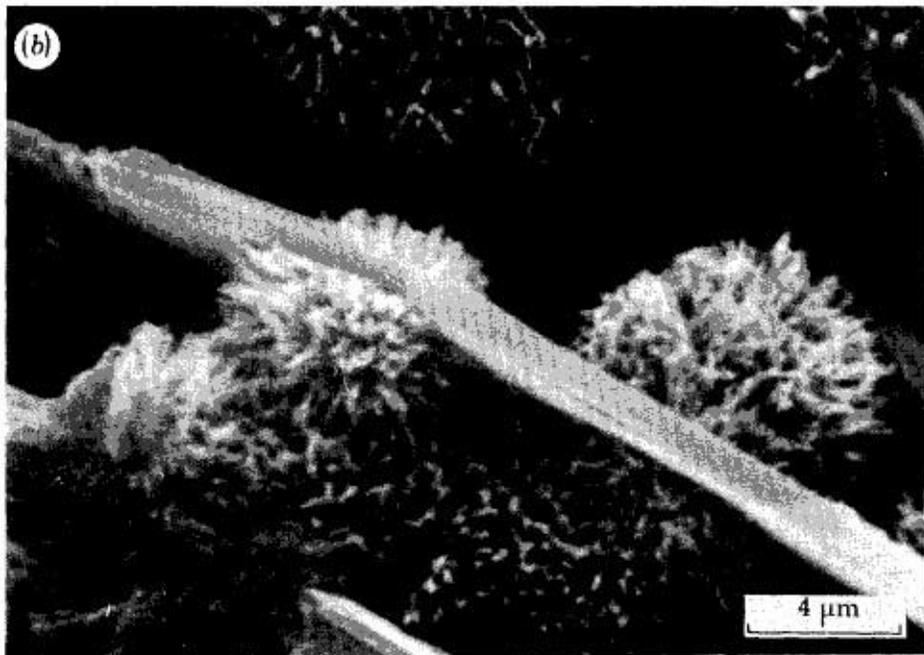


Figure 3: Scanning electron micrograph of mature paste. Calcium silicate hydrate with calcium hydroxide lathes. From Double et al., 1978.

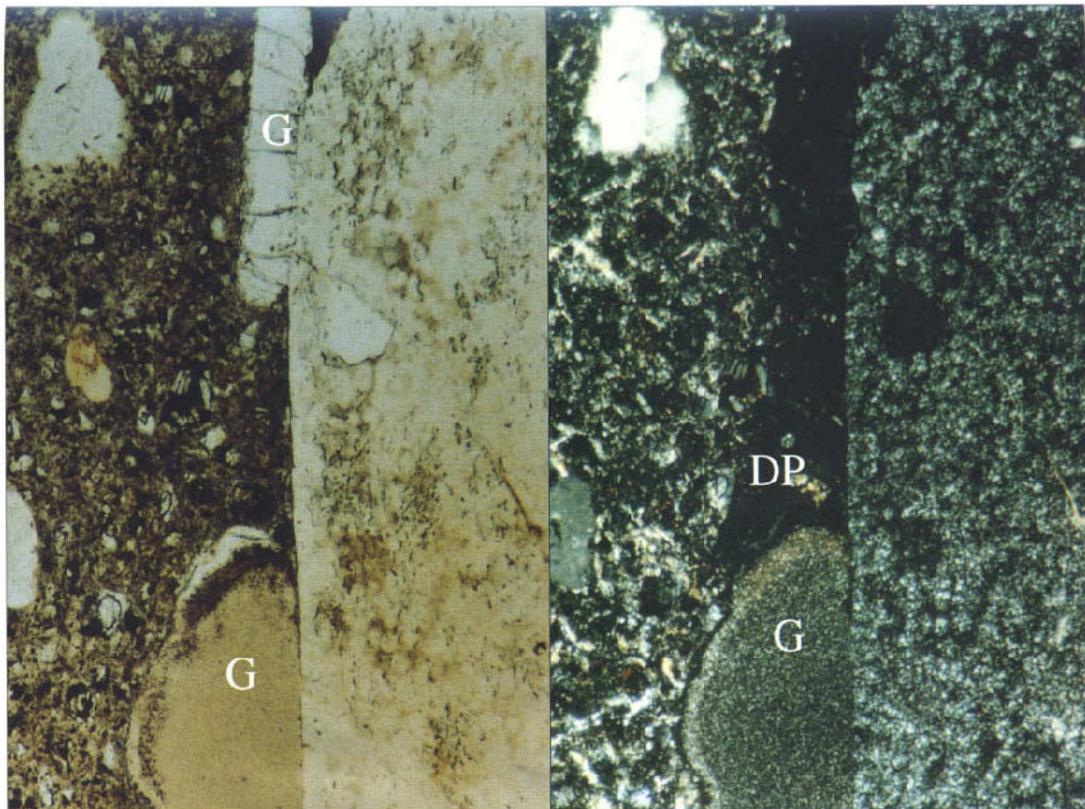


Figure 4: Width of field 0.8 mm. Chert aggregate (right) with patches of alkali silica gel (G). Crossed polar view on right: DP indicates darkened cement paste due to saturation by the gel and absorption of calcium hydroxide. From St. John et al., 1998.

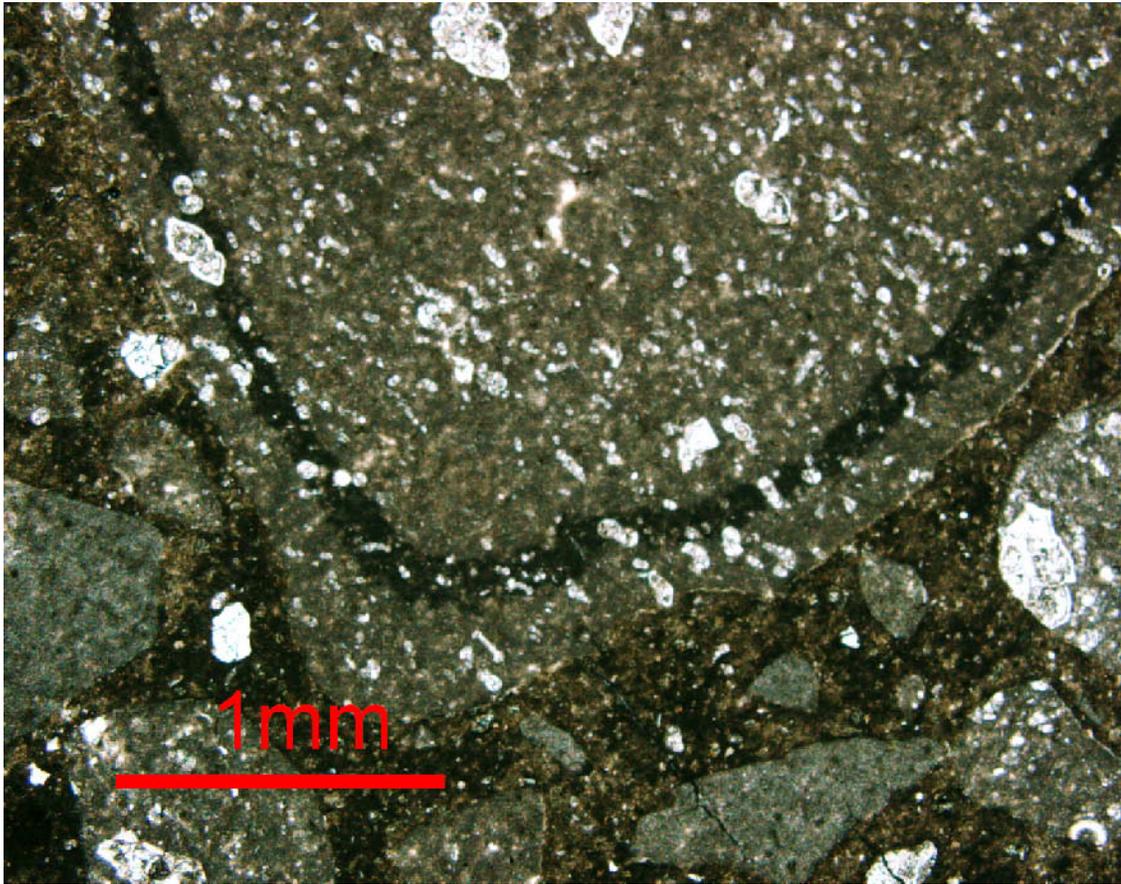
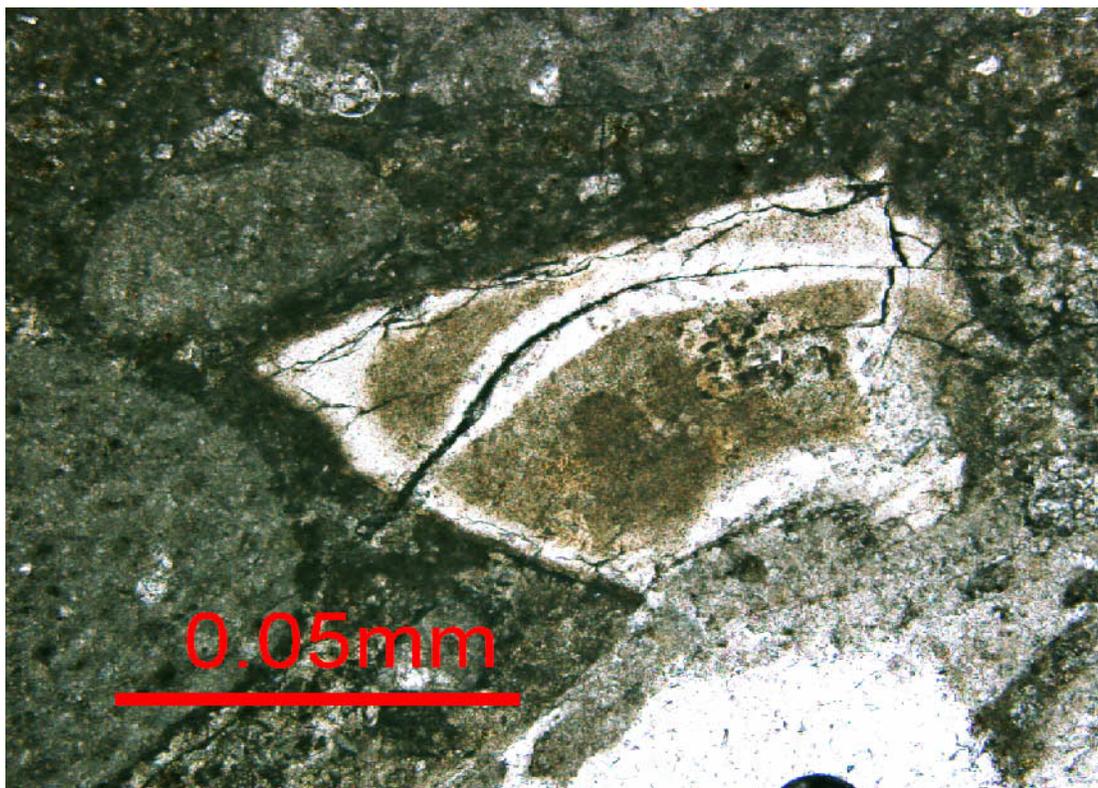


Figure 6: Limestone clast in sample 2000 with rim. Plane polarized light.

Figure 7: Fractured chert in sample 2000. Note that fractures extend into the matrix material. A) plane polarized light B) crossed polars.

A)



B)

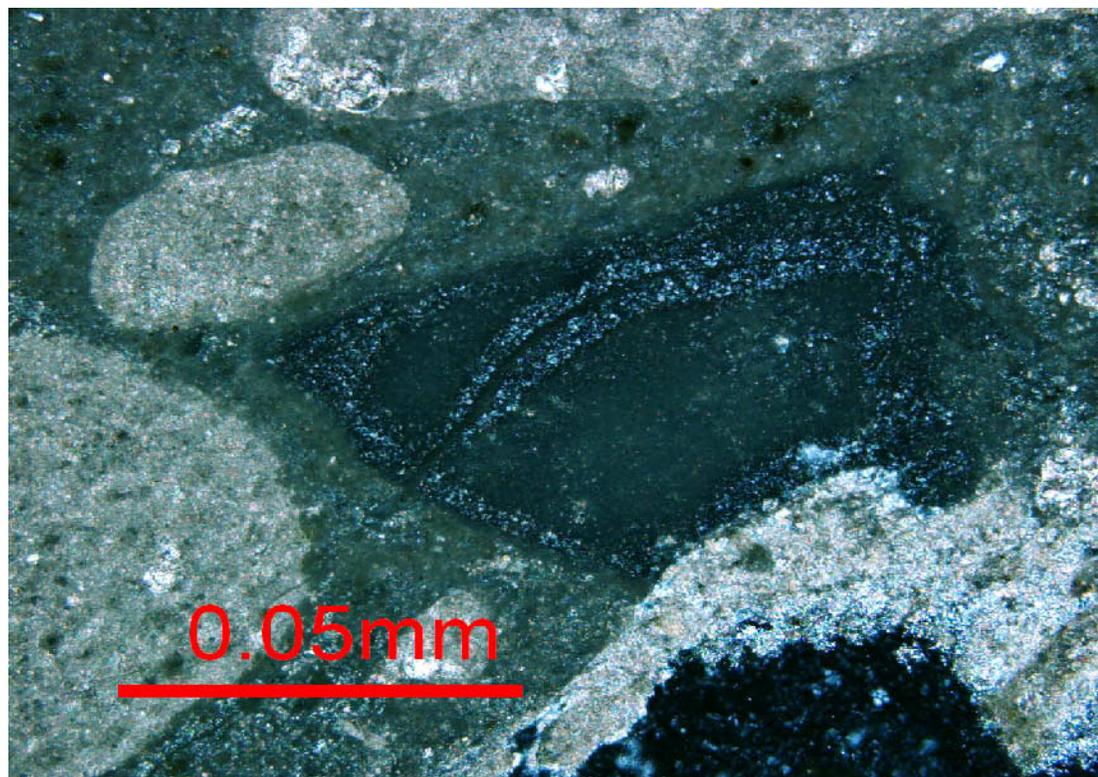
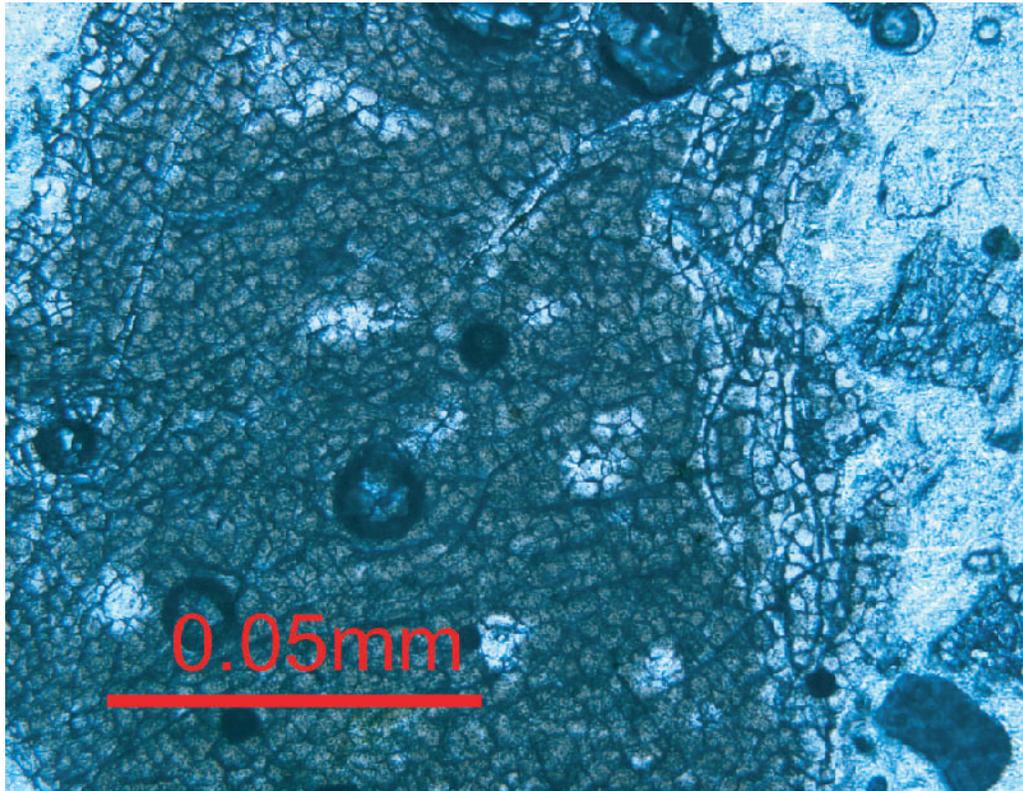


Figure 8: Jesi aggregate chert clast with both pre-existing fractures and those created during thin section preparation. A) plane polarized light B) crossed polars.

A)



B)

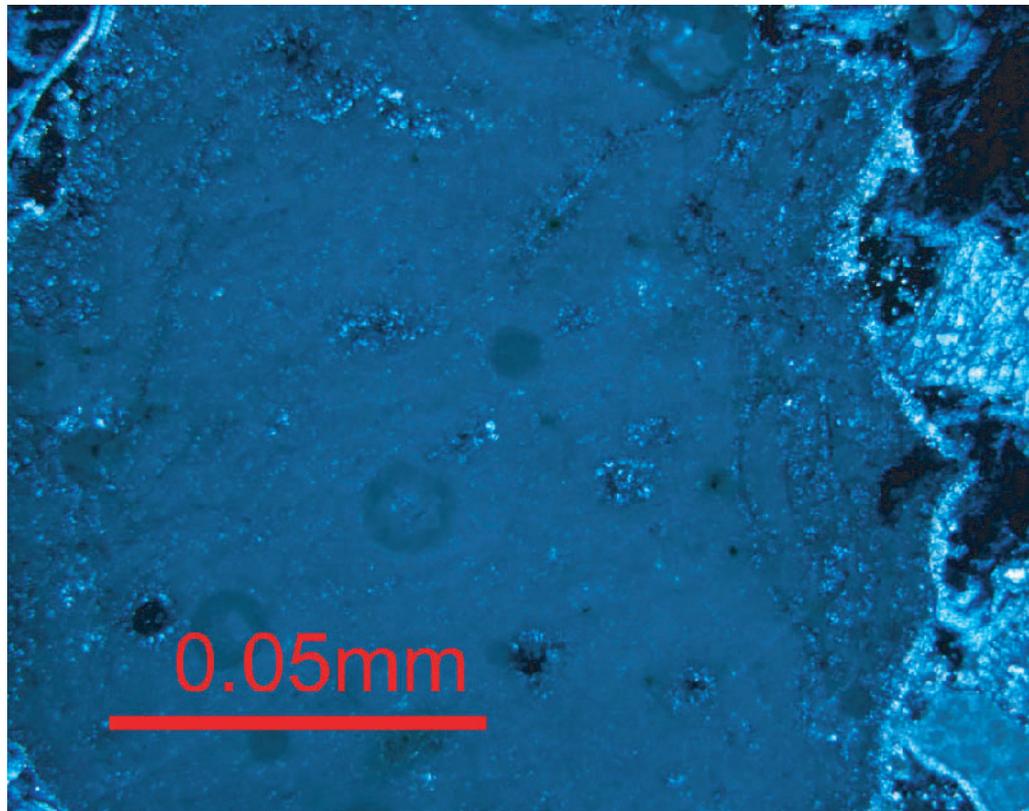


Figure 9.1: Backscattered electron micrograph of limestone clast with discolored rim in sample 2000.

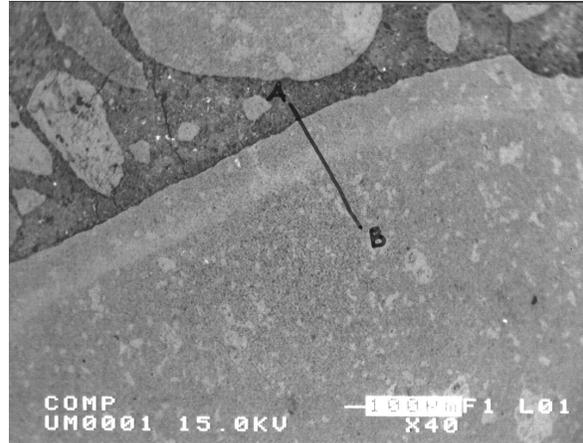


Figure 9.2: Wavelength dispersal spectrum data for transect of limestone clast in sample 2000. Note that scale varies by element.

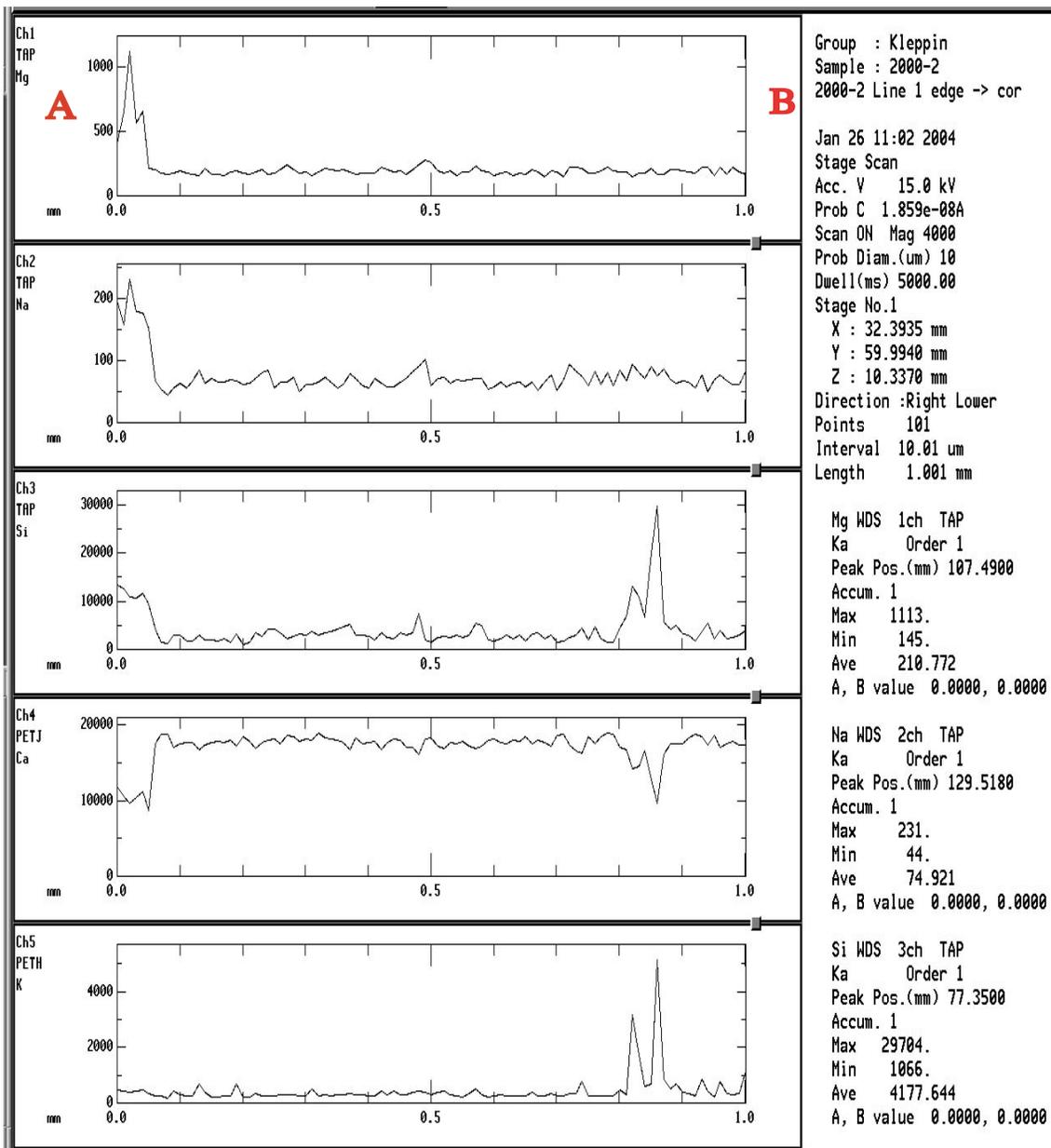


Figure 10.1: Backscattered electron micrograph of chert fracture in sample 2000. Notice probe damage on line A1-B1. This indicates the presence of volatile phases such as water.

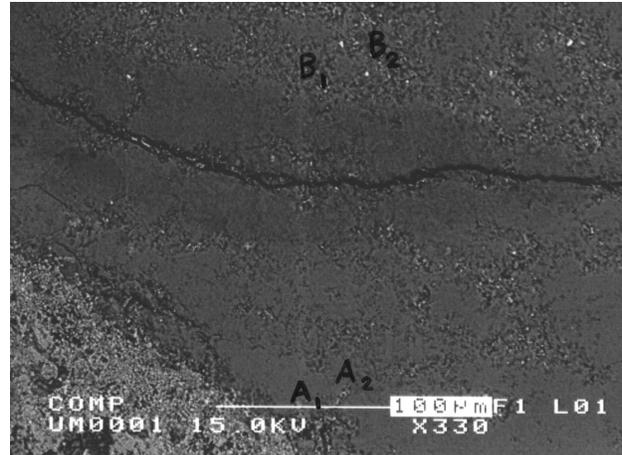
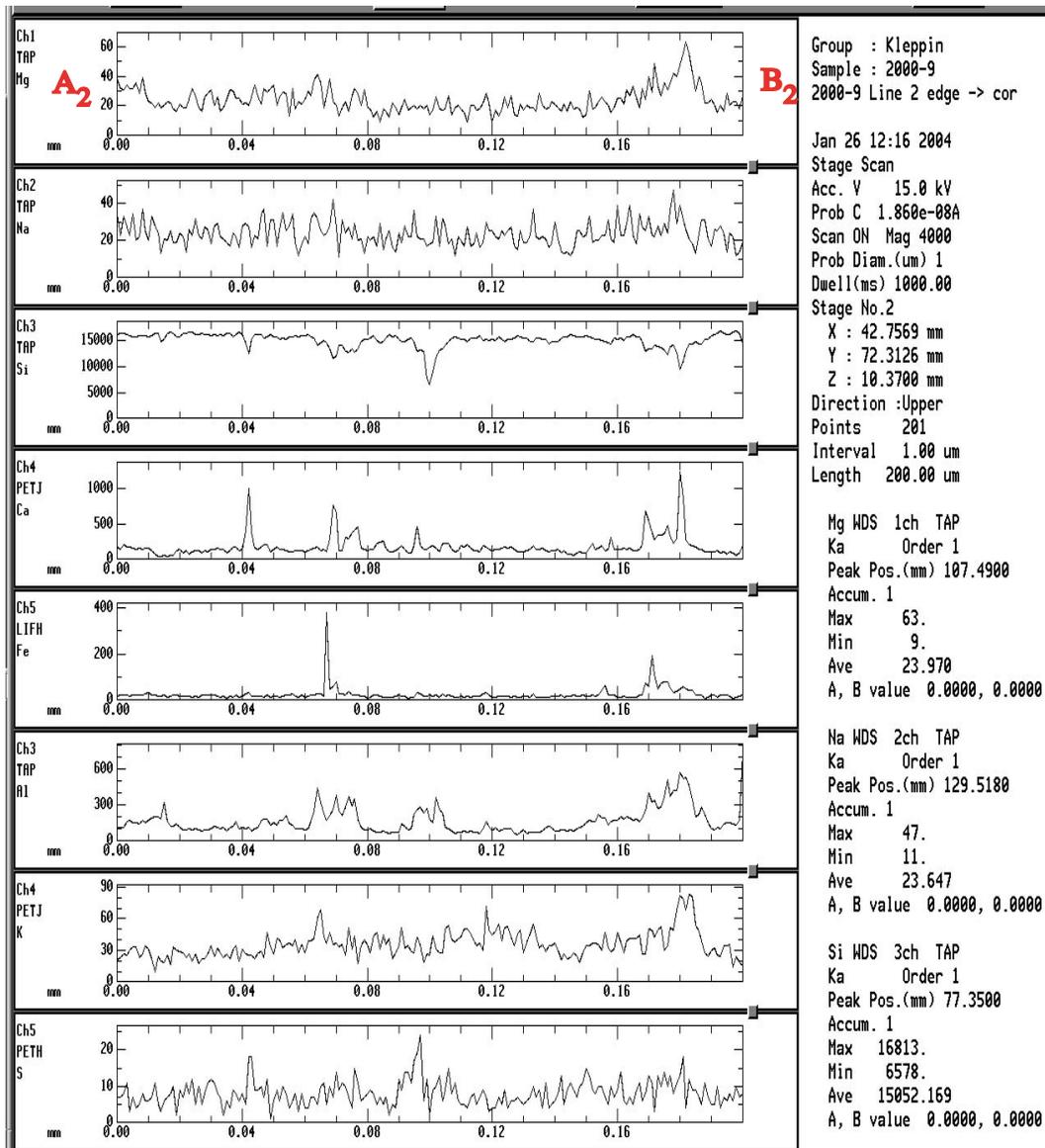


Figure 10.2: Wavelength dispersal spectrum data for transect of chert fracture in sample 2000. Note that scale varies by element.



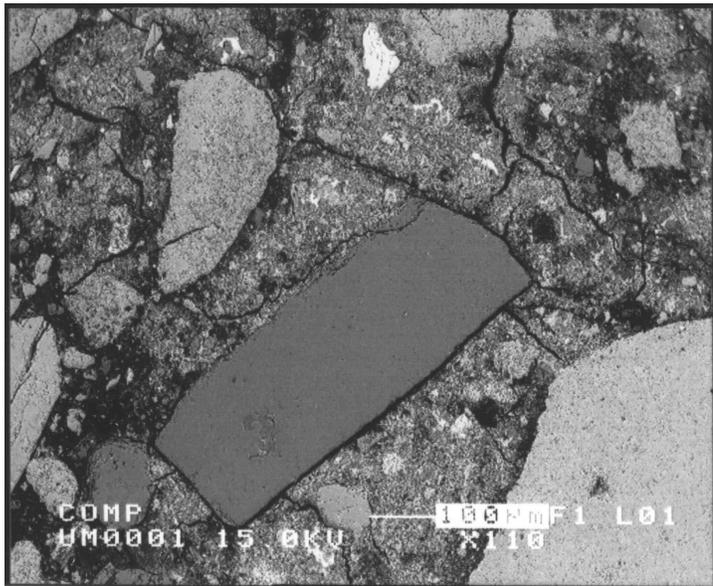


Figure 11: Backscattered electron micrograph of map cracking in sample 19--.

Figure 12: Entrained air vessicle filled with grinding debris in sample 2000. Note desiccation fracturing in aggregate and matrix. A) plane polarized light B) crossed polars.

