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Cracking and crumbling of concrete blocks in County Donegal, Ireland: A holistic approach from case studies on deleterious effects of open microstructure of blocks, phyllite aggregate, pyrrhotite Oxidation, paste carbonation, lime leaching, and internal sulfate attacks

Dipayan Jana[1]

(1) Construction Materials Consultants, Inc. and Applied Petrographic Services, Inc., Greensburg, USA, info@cmc-concrete.com

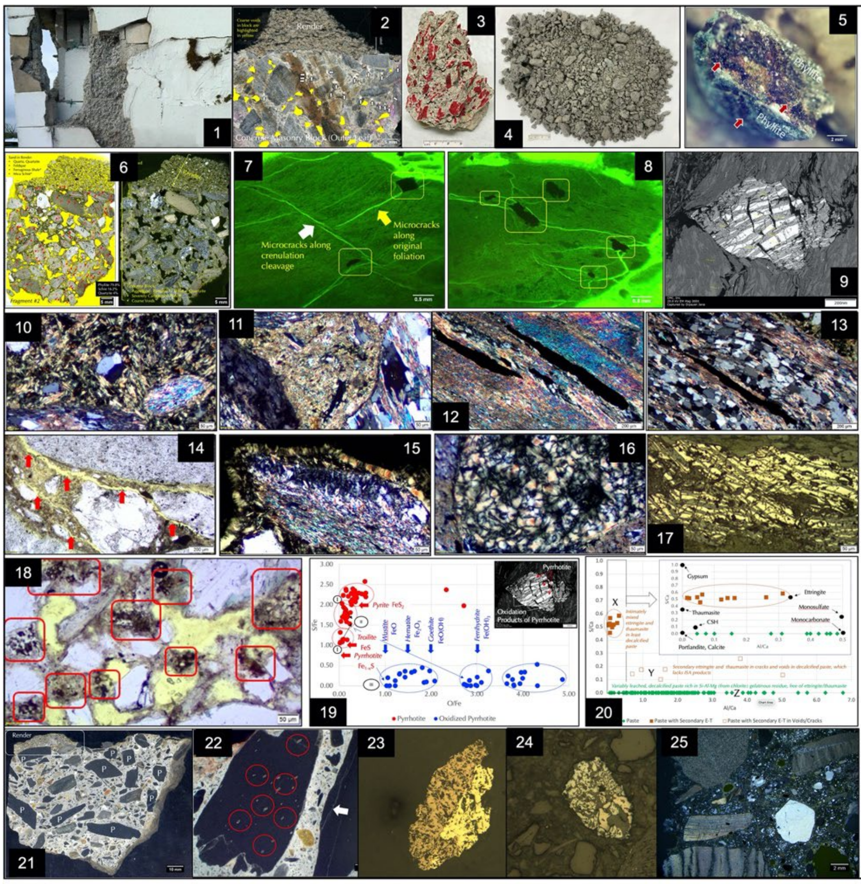
Abstract

Two different mechanisms are offered for extensive cracking and crumbling of an estimated 5000 properties in County Donegal in Ireland. One mechanism, known as the 'mica crisis' is reported to be from the use of defective concrete blocks containing excessive (free) mica in the mortar fractions derived from micaceous aggregates (mostly phyllite with subordinate mica schist, quartzite, etc.). Excess mica from abraded phyllite in paste has reportedly caused many known mica-related issues, e.g., increased water demand at a given workability, increased water absorption, increased microporosity, loss of compressive strength, reduced resistance to frost attack from high water demand, increased leaching, etc. Subsequent studies have established evidence of iron sulfides mostly in the form of pyrrhotite in the aggregates, which have caused oxidation and related expansions in the presence of moisture and oxygen followed by internal sulfate attacks (ISA) from reactions between sulfates released from pyrrhotite oxidation and cement hydration products resulting in formation of gypsum, ettringite, and thaumasite causing expansions and cracking to softening and crumbling of paste from decomposition of calcium silicate hydrate (CSH) from thaumasite attack and severe carbonation and leaching of paste. The present report has taken a holistic approach from case studies of moderately to severely crumbled blocks to sound cast-in-place foundation of homes in County Donegal to evaluate deleterious roles of open microstructure of blocks, phyllite aggregates, pyrrhotite oxidation, paste carbonation and leaching, and internal sulfate attacks for the catastrophic distress.

***Keywords**: cracking, Donegal, ISA, phyllite, pyrrhotite*

1. INTRODUCTION

The so-called 'mica crisis' in Ireland [1, 2, 3] is rightfully confirmed to be the case of internal sulfate attacks (ISA) from oxidation of iron sulfide minerals (mostly pyrrhotite, sometimes along with pyrite) in aggregates used in the defective concrete blocks [4, 5]. Studies of 1800 distressed properties from 1995 to 2010 in County Donegal found deleterious roles of pyrrhotite-bearing phyllite as the main cause of distress [5]. From the independent case studies of author on the severely crumbled down to 'powder' to moderately crumbled 'fragments' of blocks from some of the most distressed homes (Fig. 1.1 Photos 1-20), along with 'sound' cast-in-place concrete foundation of a house (Fig. 1.1 Photos 21-25) all containing same crushed pyrrhotite-bearing phyllite aggregate reportedly sourced from the same Buncrana quarry as the aggregate source for the other defective blocks, a preliminary holistic approach is taken to evaluate relative roles of: (1) open microstructure of blocks as opposed to denser microstructure of cast-in-place foundation for deeper penetration of moisture, oxygen, and CO_2 in blocks during service than in foundation, (2) easy abrasion of phyllite to expose more pyrrhotite grains to oxidation than other hosts during block manufacturing, (3) advanced pyrrhotite oxidation in blocks starting from steam curing process to easy access to moisture/oxygen during service through open microstructure of blocks, (4) deeper, pervasive carbonation through open-structured block than limited (max. 15 mm) carbonation in denser foundation, (5) preferential internal sulfate attacks (ISA) in the paste of distressed blocks but not in the sound foundation from sulfate release from pyrrhotite oxidation to cause (5a) deleterious ettringite formation (E-ISA) in the denser confined spaces of less/non-carbonated regions to cause expansions and cracking to (5b) deleterious thaumasite formation (T-ISA) in the porous, moderately carbonated regions to cause decomposition of calcium silicate hydrate (CSH) with softening and disintegration to (5c) gypsum form of ISA (G-ISA) in severely carbonated paste by replacing calcium carbonate, and (6) leaching of lime and products of ISA from continued moisture circulation throughout the open-structured block during service to re-precipitate lime and ISA products in voids and turn the paste into a silica-alumina-magnesia-based gelatinous mass with little or no cementitious property, which was already started with T-ISA to cause catastrophic crumbling of blocks across County Donegal.



1: Cracking and crumbling of one of the most distressed homes in County Donegal from where fragment shown in '2' came.
2: Soft, porous, carbonated render on a defective block having abundant interstitial voids and white secondary deposits in voids.
3: Abundant phyllite flakes (marked red) in block.
4: Severely crumbled block from another house.
5: Oxidation products of pyrrhotite caused splitting of phyllite.
6: Fluorescent dye-mixed whole slide thin section of block in PPL/XPL showing abundant pyrrhotite-bearing phyllite in porous carbonated paste.
7: Microcracks in phyllite along foliation planes and crenulation cleavages for moisture access.
8: Radial cracking from pyrrhotite in phyllite.
9: Cracking in an oxidized pyrrhotite and associated cracking in host phyllite.
10: Abundant abraded phyllite in mortar fraction - the origin of 'excess mica' hypothesis.
11: Severe carbonation of paste.
12: Pyrrhotite mostly along foliation plane in phyllite.
13: Pyrrhotite along biotite flakes in mica schist.
14: Severe microcracking in mortar fraction of defective blocks.
15: Thaumasite along aggregate-paste interface.
16: Thaumasite filling an air void.
17: Characteristic iron oxide bands in oxidized pyrrhotite.
18: Abundant residual Portland cement particles in porous, carbonated, inadequately cured render in defective blocks.
19: SEM-EDS analyses of pyrrhotite, pyrite, and oxidized products in S/Fe vs O/Fe atomic ratio plots.
20: SEM-EDS analyses of compositional variations of paste and various secondary deposits in S/Ca vs. Al/Ca plots.
21: Sound cast-in-place concrete foundation containing abundant pyrite and pyrrhotite-bearing phyllite and mica schist.
22. Fine, disseminated iron sulfide grains in phyllite in foundation concrete.
23: Interlocked pyrrhotite and pyrite in phyllite in foundation concrete.
24: Oxidized pyrrhotite in mortar fraction.
25: Abundant phyllite aggregates in foundation concrete with iron sulfide grains. Interior paste is non-carbonated.

Figure 1.1: A microstructural collage of defective concrete blocks (Photos 1 to 20) and sound cast-in-place foundation (Photos 21 to 25) from County Donegal, Ireland.

2. METHODOLOGIES

All samples were examined by: (1) polarized-light microscopy (reflected-light microscopy of polished thin and solid sections, transmitted-light microscopy of polished thin sections) for iron sulfide minerals, oxidation products, aggregates' mineralogies/textures, paste compositions/microstructures/alterations, and secondary deposits, (2) SEM-EDS studies of polished thin/solid sections for further characterization of phases detected in optical microscopy, (3) XRD studies of bulk samples and extracted aggregates for detection and quantifications of iron sulfide minerals, aggregate mineralogies, and ISA products, (4) XRF and combustion IR for major element oxide compositions and total sulfur content (S_T), (5) thermal analysis for sulfate/carbonate phases, and (6) ion chromatography of filtrates of deionized water-digested samples for water-soluble sulfate contents. Details can be found in Jana [6].

3. RESULTS

Crumbling in one of the most distressed homes in County Donegal (Fig. 1.1 Photo 1) examined by author was the result of multiple episodes that started with the use of defective concrete blocks having: (1) abundant easily splitable phyllite aggregates (as high as 80% by volume of coarse aggregate, Fig.

1.1 Photos 2, 6), along with (2) overall porous, high water-cement ratio (*w/c*), and low cement content (4% [3]) nature of blocks leaving a lot of interstitial spaces for migration of moisture, oxygen and CO_2 through the renders to the blocks especially at the outer leaf to cause pyrrhotite oxidation, paste carbonation, ISA, and leaching/re-precipitation.

Phyllite occurred as low-grade, fine-grained metamorphic rock of Precambrian Dalradian Supergroup consisting of major amounts of interlayered muscovite, chlorite and subordinate amounts of very fine-grained silty quartz and alkali feldspar all in parallel layered arrangements to form the typical foliation or sheet-like flakes and characteristic crenulation cleavages of deformed flakes (Fig. 1.1 Photos 10-12). Weak zones along foliation planes and crenulation cleavages provided crisscross intersecting pathways for migration of moisture and oxygen to pyrrhotite (Fig. 1.1 Photo 7). Muscovite and chloride are non-swellable sheet silicates but their presence as easily breakable foliated sheets in phyllite along with their inherent finer grain size than schist have contaminated the mortar fractions of blocks with abraded phyllite flakes (>10% to as high as 50%, by paste volume) to increase the water demand at a given workability and reduce the compressive strength. After phyllite, coarser-grained mica schist is detected at subordinate (15-20%) amount consisting of parallel alignments of muscovite mica, biotite, chlorite, deformed quartz, and alkali feldspar grains (Fig. 1.1 Photo 13). Only a minor (1-5%) amount of noticeably denser and non-foliated coarse-grained metaquartzite aggregate is found, which, if were used as the primary aggregate would have drastically reduced the observed disintegration of blocks let alone to expose pyrrhotite grains to oxidize.

Abundant pyrrhotite grains in phyllite (sizes from < 1 mm at long to <0.5 mm at short directions, Fig. 1.1 Photos 6-9) have acted as the effective sites for expansion from oxidation during service especially at the moist and alkaline (pH >10, less to non-carbonated) conditions of blocks. Some prior oxidations, however, may have occurred in geologic formation and during storage in the aggregate stockpile. Pyrrhotite grains are detected mostly in phyllite as opposed to mica schist or metaquartzite as (a) fine-grained isolated disseminated irregular-shaped to subhedral equant grains (Fig. 1.1 Photo 7) to (b) mostly elongated grains aligned along the dominant foliation planes (Fig. 1.1 Photo 12), which shows extensive reddish-brown oxidation products (e.g., goethite, ferrihydrite, Fig. 1.1 Photo 5) causing further cracking, splitting, and disintegration of phyllite. In situ oxidation of pyrrhotite has caused further splitting and crumbling of phyllite (Fig. 1.1 Photos 8,9) especially since most pyrrhotite grains have crystallized along the prevailing foliation planes where the inherent phyllitic texture of foliation and deformed (crenulation) cleavage planes provided pathways for ready migration of moisture to facilitate oxidation. Additionally, spectacular radial cracks are often seen from oxidized pyrrhotite grains in phyllite (Fig. 1.1 Photos 8, 9) as a testament of *in situ* expansion from pyrrhotite oxidation. Reddish-brown oxidized pyrrhotite products are preferentially noticed between the greenish sheened (from chlorite) foliated sheets where expansive oxidation reactions have further disintegrated the phyllite. Pyrrhotite contents in phyllite aggregates varied from 0.75 to 1.5 percent, by volume. Pyrrhotite is associated with pyrite though no evidence of oxidation of pyrite, or its subsequent sulfate attack (as found in the neighboring County Mayo from framboidal pyrite) was found in the present study.

S_T varied from 0.5 to 1% by mass in distressed blocks and sound foundation depending on the pyrrhotite and pyrite contents, which after converting to aggregate sulfide contents for appropriate aggregate contents are a factor of 5 to 10 times higher than the maximum allowable sulfur content of 0.1% as per EN 12620 specification. At least for the foundation, a high S_T did not necessarily transform to high risk, which amongst various reasons is due to the abundance of non-reactive (blocky) form of pyrite, which has contributed to the lion's share of S_T, and non-reactive finely disseminated form of pyrrhotite.

Fig. 1.1 Photos 19 and 20 show SEM-EDS analysis of compositional variations of pyrrhotite with oxidation products, and paste with secondary deposits, respectively. XRD studies showed both pyrite and pyrrhotite in blocks and foundation but higher amounts of pyrrhotite in blocks leading to higher risk along with indication of potential variations in pyrrhotite contents across the quarry.

Along with aggregate disintegration, mortar fractions of blocks (Fig. 1.1 Photos 10, 11, 14) became the junkyard of (1) abundant abraded fractions of phyllite, (2) oxidized pyrrhotite grains, (3) products of carbonation, (4) lime-poor silica-alumina-magnesia gel from carbonation to decalcification (magnesia was from chlorite decomposition), (5) scattered products of E/T/G-forms of ISA either in least leached/carbonated paste, or as (6) innocuous secondary deposits lining air voids and pores from dissolution and reprecipitation in the decalcified regions of paste. All these products are initially characterized from optical microscopy but best diagnosed during subsequent SEM-EDS studies.

Since pyrrhotite-bearing phyllite occupied much larger volumes (80%) of blocks than the mortar fractions (<10%), distress from aggregate disintegration by pyrrhotite oxidation contributed to the larger part of distress at the initial stage to cause initial cracking, which was followed by subsequent disintegration of the lower volume mortar fraction mostly from carbonation, ISA, and leaching to cause eventual softening and crumbling of blocks.

For the sample from cast-in-place foundation, nonreactive pyrite is more abundant than pyrrhotite, where the former contributed to the lion's share of S_T and the latter mostly occurred as nonreactive fine disseminated grains in phyllite (Fig. 1.1 Photo 22) instead of along foliations, and lesser in the mortar fractions where it shows some oxidation (Fig. 1.1 Photo 24), which is consistent with lesser amount of abraded phyllite in the mortar fraction (Fig. 1.1 Photo 25) than found in defective blocks. Characteristic 'striated' appearance of oxidized pyrrhotite grains having iron oxide bands in iron sulfide body so common in the blocks (Fig. 1.1 Photos 9, 17) are virtually absent in the foundation (Fig. 1.1 Photo 23). Carbonation was restricted to the top 15 mm mostly in a porous cementitious coating on concrete, where secondary ettringite is found in voids. Evidence of E-ISA, T-ISA, or G-ISA are not found in the interior concrete, nor any cracking, which are due to the inherent denser microstructure of concrete along with the absence of moisture during service. Cases from Canada and US, however, showed that denser microstructure alone cannot prevent the distress if foundation were exposed to moisture during service.

4. DISCUSSIONS

Sulfates released from pyrrhotite oxidation as sulfuric acid create an ideal scenario for ISA from deleterious formation ettringite (E-ISA) in the confined spaces in paste from reactions with monosulfates and associated expansions and cracking. E-ISA, however, is more common in the denser and less carbonated concrete, e.g., as seen in numerous residential concrete foundations in the eastern Connecticut [6,7] than in the defective concrete blocks that are inherently porous with a high void content (for use of a low cement content mix), and a porous, high *w/c* paste (for the high-water demand of abraded phyllite). Extent of distress from pyrrhotite oxidation and subsequent forms of ISA are essentially controlled by the host rock for pyrrhotite and whether the distress is occurring in a dense concrete microstructure (e.g., cases in eastern Connecticut or Canada [6,7,9]), or in an inherently porous microstructure of concrete block as in the present case.

In the distressed blocks, sulfates released from pyrrhotite oxidation did cause E-ISA but mostly in the moist condition in initial non-carbonated low-volume porous paste, and in intergranular void spaces and air voids as the first form of ISA, whose remains became limited as the porous paste became dried and carbonated when thaumasite-form of ISA (T-ISA) became evident especially during the cold weather conditions (at 5 to 15°C). Localized occurrence of gypsum is reported in the severely carbonated paste by reaction with calcite as the final form of ISA (G-ISA) at the high sulfate areas [4]. Though not detected in the presently examined block fragments probably for advanced dissolution, but G-ISA is found in the study of other distressed blocks by Leemann et al. [4] and is, indeed, very common in many other cases in Ireland, e.g., causing cracking of defective blocks in County Mayo containing framboidal pyrite in limestone aggregates [1] or devastating building heaves in Dublin constructed on carbonate mudstone fill containing framboidal pyrite where reactions between sulfates released from pyrite oxidation and calcite in the host rock have caused expansive formation of gypsum [8].

High intergranular void contents and low volume, porous, high *w/c* paste of blocks have caused effective carbonation of paste especially when relative humidity was in the range of 60-80% to convert original calcium hydroxide and CSH components to fine-grained calcite and hydrated silica-alumina gel thereby providing the seeds for T-ISA. Carbonation occurred more effectively in the relatively drier inner leaf and during intermittent dry periods in the outer leaf, which itself at the advanced stage can cause severe loss of strength from decomposition of CSH. Deleterious effects of carbonation-induced T-ISA, however, are more pronounced at the early stages of carbonation and in the least decalcified regions. Severe carbonation (pH <10) and lime leaching to the point of silica-alumina-gel formation from original CSH either prevent T-ISA or restrict secondary thaumasite formation mostly in the porous regions and as linings in air voids and cracks simply from dissolution, redistribution, and reprecipitation of available dissolved sulfate and carbonate ions – as seen in the severely disintegrated blocks. Such three-stage alterations of CSH, i.e., first by carbonation, then by subsequent T-ISA, and finally by severe leaching/decalcification has caused severe disintegration and crumbling of blocks. T-ISA, however, is more pronounced in the distressed blocks than in the foundation sample (as also not seen in distressed foundations in eastern Connecticut, USA [6,7]), which is directly related to much denser microstructure of foundation concrete to prevent severe carbonation (or any other source of carbonates). Carbonates released from paste carbonation during drier periods (at 60-80% relative humidity) along with sulfates released from pyrrhotite oxidation during wet periods have caused T-ISA preferentially in the outer leaf to cause its higher extent of damage than the inner leaf.

Distresses from E/T-ISA, however, are less evident in the severely carbonated, porous, silica-alumina-rich gelatinous regions of paste where products of ISA are mostly found as secondary deposits in coarse voids (as interlayered secondary ettringite and thaumasite fibers, Fig. 1.1 Photo 16) from dissolution and re-participation, whereas in the least de-calcified regions E/T-ISA products are often found mixed within the paste to implant seeds for potential expansions. Distresses from E/T-ISA, however, are inherently restricted for the low (<10%) paste volumes of blocks and even more so only in the moderately carbonated and less decalcified paste regions. The outcome, however, is severe crumbling of blocks.

Abundant pyrrhotite provided the starting ingredients for ISA, foliated nature of phyllite provided ideal pathways for entry of moisture and oxygen to release sulfates for E/T-ISA, porous microstructure of blocks provided pervasive carbonation and released carbonates and silica gel for T- ISA, but the extent of distress from E/T-ISA are controlled by the abundance of pyrrhotite (for sulfates) in the phyllite host, paste volume, and the degree of leaching and carbonation (for carbonate and silica source for thaumasite). Moist conditions in the outer leaf promoted pyrrhotite oxidation and sulfate release to cause E-ISA distress from expansive ettringite formation in the noncarbonated paste leading to initial cracking, whereas subsequent T-ISA at moderately carbonated paste at colder and relatively drier conditions mostly contributed to crumbling. Relatively drier conditions in the inner leaf promoted advanced carbonation but intermittent drier conditions between moist seasons in the outer left promoted cyclic formation of E-ISA during moist conditions to T-ISA during intermitted carbonation at drier and colder conditions. The end results of carbonation and T-ISA are a paste of little or no cementitious property eventually causing mass-scale crumbling of blocks. Effects of pyrrhotite oxidation are more towards initial cracking and crumbling of blocks, whereas that of carbonation and T-ISA are towards eventual decomposition of paste to cause large-scale crumbling of blocks. Not one single factor alone has had the lion's share for catastrophic failure of houses – as many as six different factors are discussed here, which have worked together to cause the progressive damage. *Pyrrhotite was the undoubted 'cancer cell' in the blocks whose deleterious effect was initiated with moisture and spread rapidly through interactions of other five factors mentioned in the title and discussed here*. *It is time to take a holistic approach in Ireland instead of polarized views of wrongfully advertised mica-only to rightfully determined ISA-only theories*.

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5. REFERENCES

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After CT-MA in US and Quebec, Canada

Ireland has become the Epicenter of Pyrrhotite Nightmare!

Map Cracking - Pattern Cracking - Disintegration of Blocks - Outward Bowing of Outer Leaf - Wide Vertical/Horizontal Cracks - Window/Door Displacement - Blown Render

Crumbled block samples from Houses 1 to 3 and a sound foundation sample from House 3

An estimated 5,000 properties are affected in County Donegal

www.cmc-concrete.com

www.petrography.net

Some severely distressed homes in County Donegal, Ireland from where samples for this study were retrieved

Two Different Notions for Distress

Field Distress

Extensive Cracking and Crumbling of Concrete Blocks

from

Culprits Presented

Excessive Mica in the Blocks

(Expert Panel's Report 2017)

Mica Action Group

Internal Sulfate Attacks (ISA) of Paste from Oxidation of Iron-Sulfide Minerals in Blocks

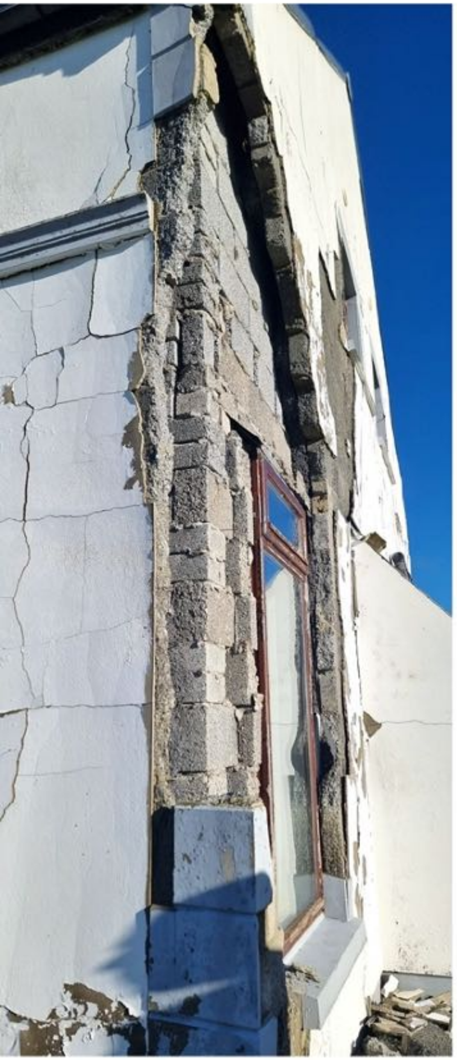
(Leemann et al. 2022)

No Pyrite-Pyrrhotite-ISA Action Group?

Interpretations Offered

- Loss of Compressive Strength
- High Water Demand from Excess Mica
- High Water Absorption
- Expansion from Wetting and/or Freezing of Water-Saturated Blocks
- Low cement, high void contents in mix

- Expansion from Oxidation of Iron Sulfide (pyrrhotite, framboidal pyrite)
- Paste Disintegration from ISA from Sulfates Released from Iron Sulfide Oxidation Causing Formation of Ettringite, Thaumasite, and Gypsum



A *Holistic Approach*

On investigation of: Cracking and Crumbling of Concrete Blocks in County Donegal, Ireland

1. **Open Microstructure of Blocks** — *The Porous Body!*
2. **Easily Abradable Phyllite Aggregate** — *The Weak Organ!*
3. **Oxidation of Pyrrhotite** — *The Cancer Cell!*
4. **Carbonation, Leaching and Internal Sulfate Attacks (ISA) of Paste** — *The Polluted Blood!*
5. **Poor Quality Sand-Cement Render** — *The Weak Skin!*

Dipayan Jana
Construction Materials Consultants, Inc. and
Applied Petrographic Services, Inc., Greensburg, PA USA
info@cmc-concrete.com

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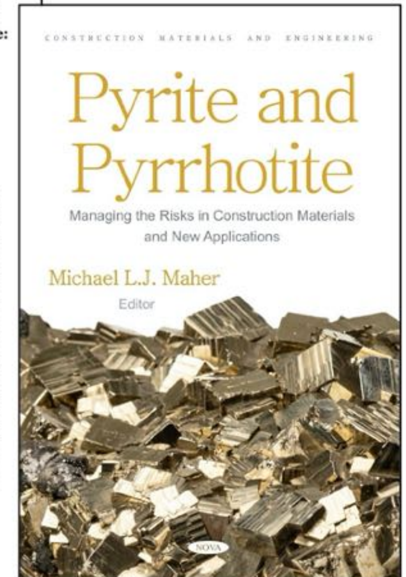
4. This work is dedicated to the Homeowners - Deirdre McLaughlin (Ireland), Paddy Diver (Ireland), Sharon Moss (Ireland)
5. Petrographer and Lab tech at CMC

Dedication

Michael L.J. Maher (1951-2022)

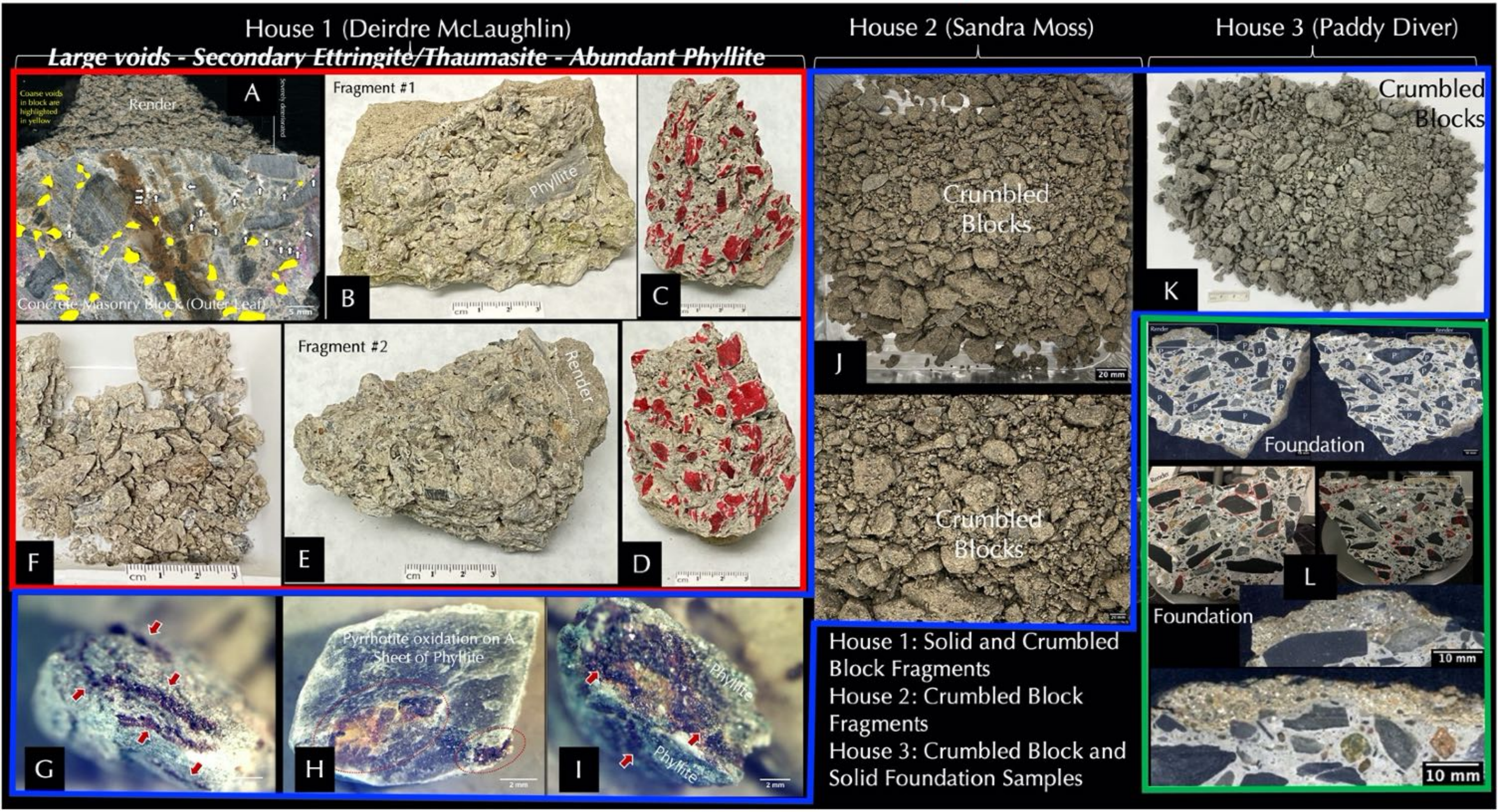
Industry Publications



All these published articles along with this entire presentation can be downloaded from www.cmc-concrete.com/pyrrhotite-crumbling-foundations

Pyrrhotite Research at CMC was not funded by any external groups

From Solid Fragments to Completely Disintegrated Samples of Blocks and A Sound Cast-in-Place Foundation Sample Received



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Some Results of Blocks: S_T 0.5-1% >> 0.1% limit of EN 12620 with Pyrrhotite; 80% Phyllite, 15-20% Mica Schist; up to 50% abraded phyllite in mortar fraction; 0.75-1.5 vol.% Pyrrhotite in Phyllite; < 10 vol.% Mortar Fraction; 5 vol.% Paste

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Extensive State-of-the-Art Laboratory Facilities For Iron Sulfide Research

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Petrographic Sample Preparation Lab

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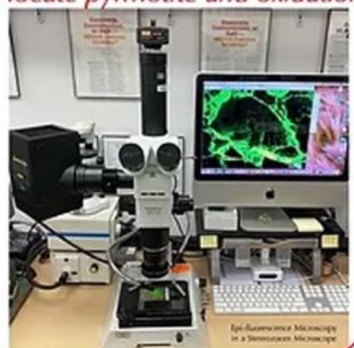
For Regular Aggregate Evaluation for Iron Sulfide

Six Common Tests

Combustion IR
for
Total Sulfur Content
To suspect pyrrhotite

Stereo-Microscopy
for
Lapped Section Petrography
To locate pyrrhotite and oxidation



Petrographic Microscopy
for
Thin Section Petrography
To locate pyrrhotite and diagnose the distress

Scanning Electron Microscopy & X-ray Microanalysis
for
Microstructural evidence of pyrrhotite oxidation and resultant products and distress

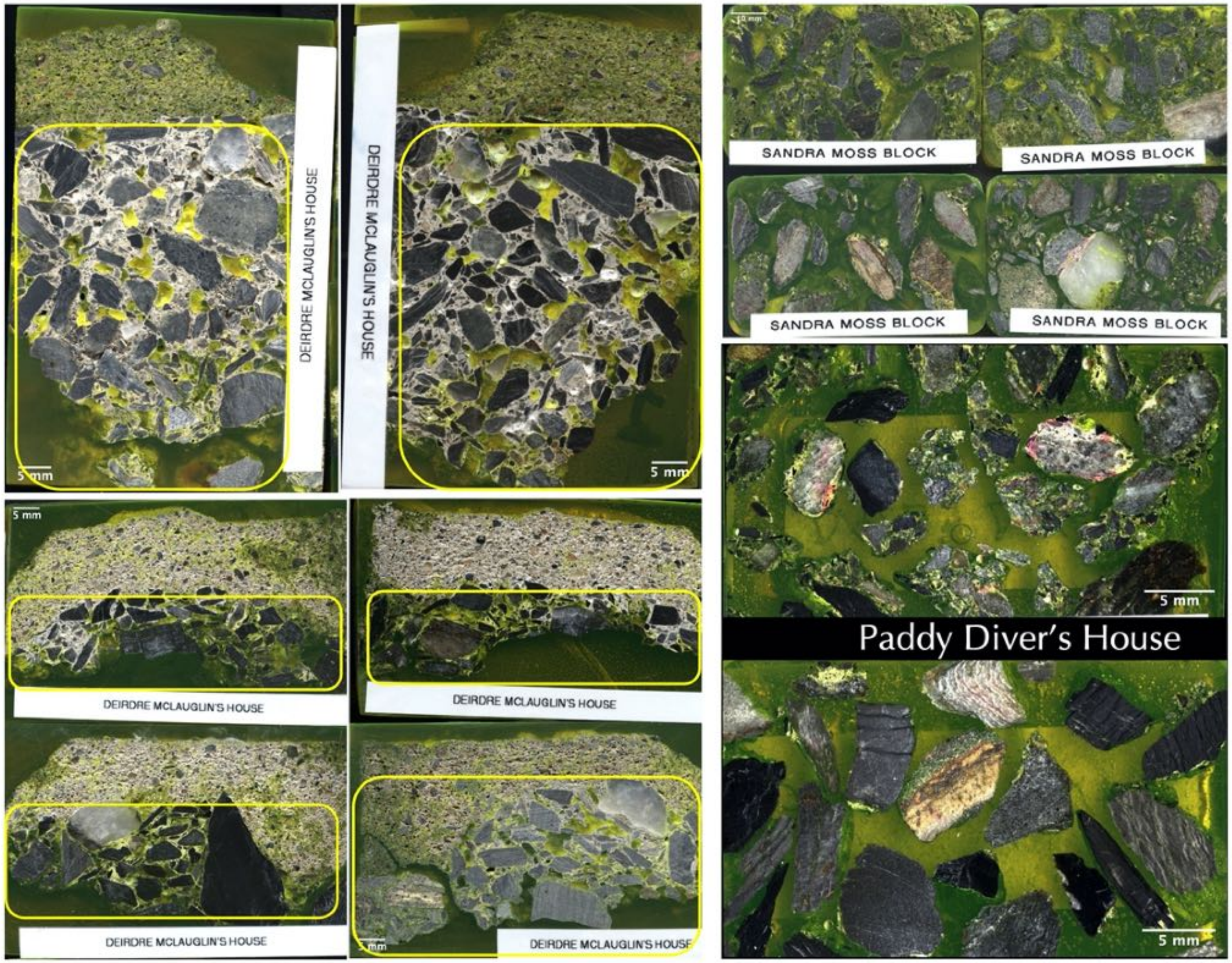
X-ray Diffraction
for
Detection and Quantification of Pyrrhotite & products of oxidation and internal sulfate attack

X-ray Fluorescence Spectroscopy
for
Sulfur Content and Speciation

Fluorescent Epoxy-Impregnated Polished Solid Sections of Blocks

RL Stereo-Microscopy   Ore Microscopy   SEM-EDS

Sample Preparation

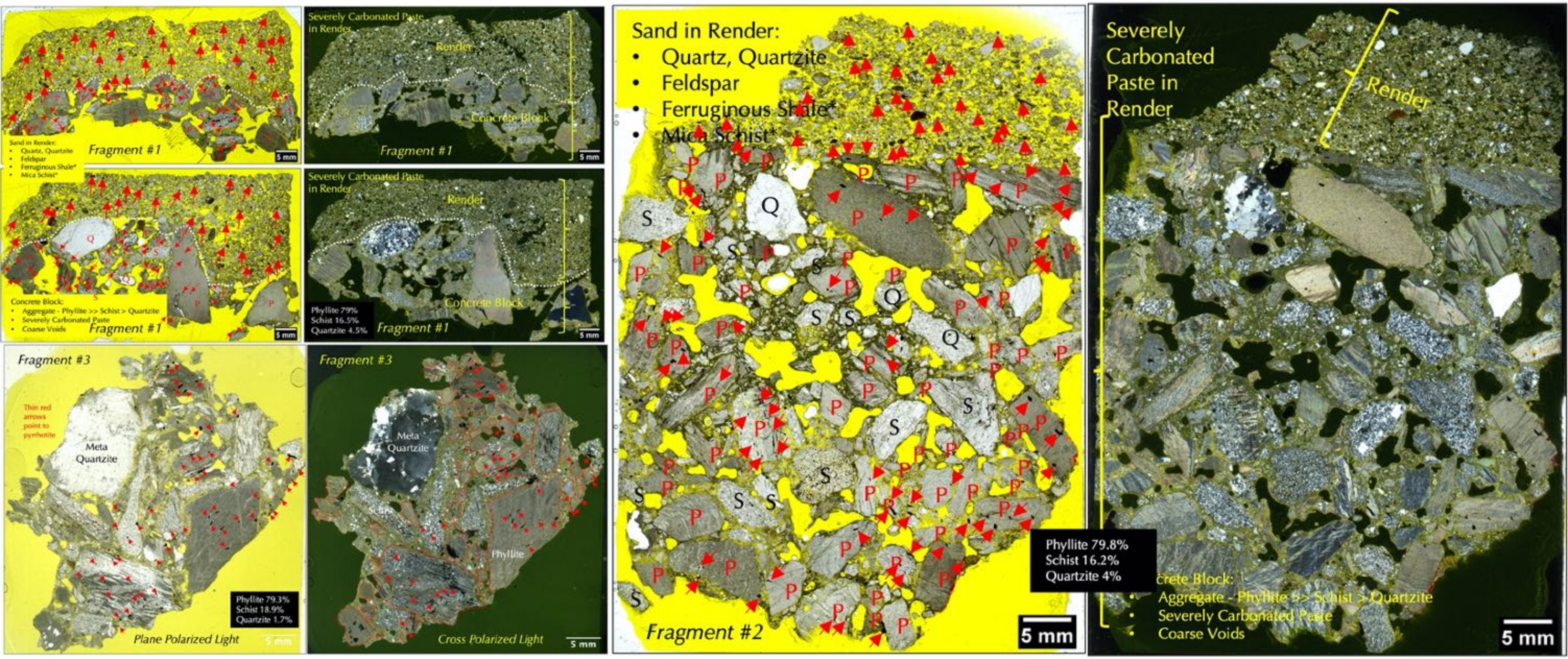


Fluorescent epoxy encapsulated polished sections for examination in reflected-light stereozoom microscope, epifluorescent stereo/petrographic microscope, and SEM-EDS

Fluorescent Dye-Mixed Epoxy-Impregnated Three Thin Sections of Blocks from House 1

PPL Scans - Abundant Coarse Voids + Abundant Finely Disseminated Pyrrhotite

XPL Scans - Phyllite > Mica Schist + Widespread Carbonation



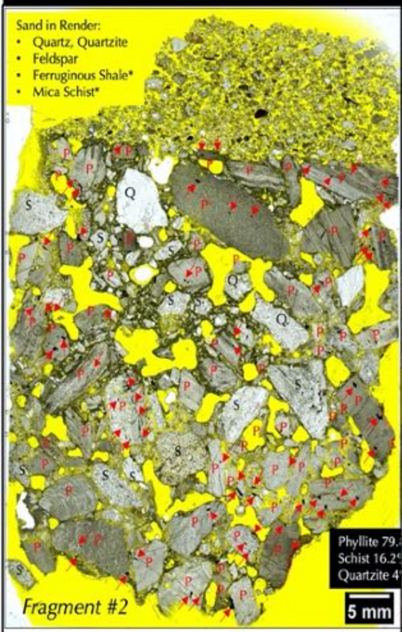
1. Phyllite is the most abundant aggregate, which is a metamorphosed claystone/mudstone/shale, which is followed by schist (mica-chlorite-schist, mica-schist), and metaquartzite.
2. Pyrrhotite, mostly occurring as disseminated grains are mostly concentrated in phyllite (all thin red arrows point to pyrrhotite).
3. Fine grain size of muscovite-chlorite-quartz in phyllite, foliation planes from parallel arrangement of grains to form planes of weakness (cleavage) and further deformation of cleavage to form 2nd series of weak planes (crenulation cleavage) make phyllite susceptible to flaking, water absorption and expansion during wetting or freezing to create microcracking (shown later in fluorescent images).

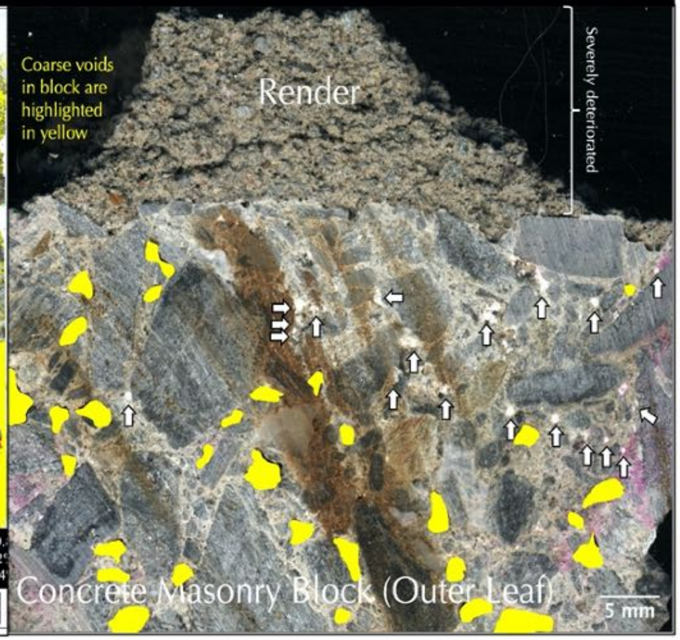
Fluorescent dye-mixed epoxy-impregnated thin sections of defective blocks scanned on transparent flatbed scanner with one or two perpendicular polarizing filters for PPL & XPL Views

1st Culprit! - Open Microstructure of Blocks for Easy Moisture Entry

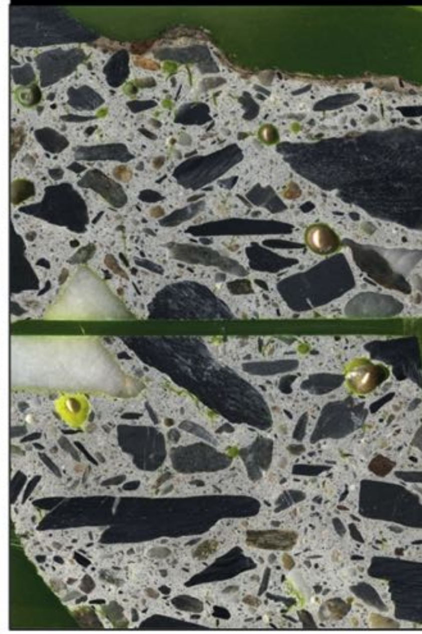
Defective Blocks (High Void Content, High w/c of Paste)
vs.
Sound Cast-in-Place Foundation (Low Void Content, Dense low w/c Paste)

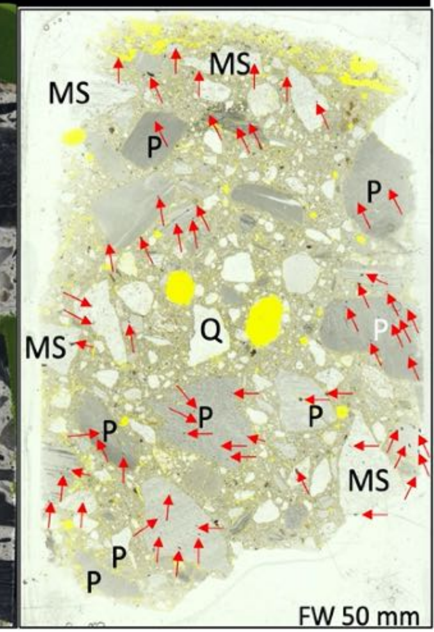
Defective Block **Open Microstructure**	**Sound Cast-in-Place Foundation** **Dense Microstructure & Lack of Moisture**





Needed Full Block Epoxy-Encapsulation to Improve Integrity





Sample was Dense Enough for just Surface Impregnation

Defective Blocks & Sound Foundation Contained
- Pyrrhotite (and Pyrite) as well as Phyllite-Mica Schist

Fluorescent dye-mixed epoxy-impregnated whole-slide scans of thin sections of defective blocks and cast-in-place foundation

2nd Culprit - Abundant Easily Abradable Phyllite - The Weak Organ!

Aggregates from the Dalradian Supergroup from 700 Ma old Mountain Building Event (Grenvillian Orogeny)

Two Sets of Textural Microcracks along ***Foliation Planes*** and ***Crenulation Cleavages*** provided easy entry for Moisture/O_2 for Iron Sulfide Oxidation

↓

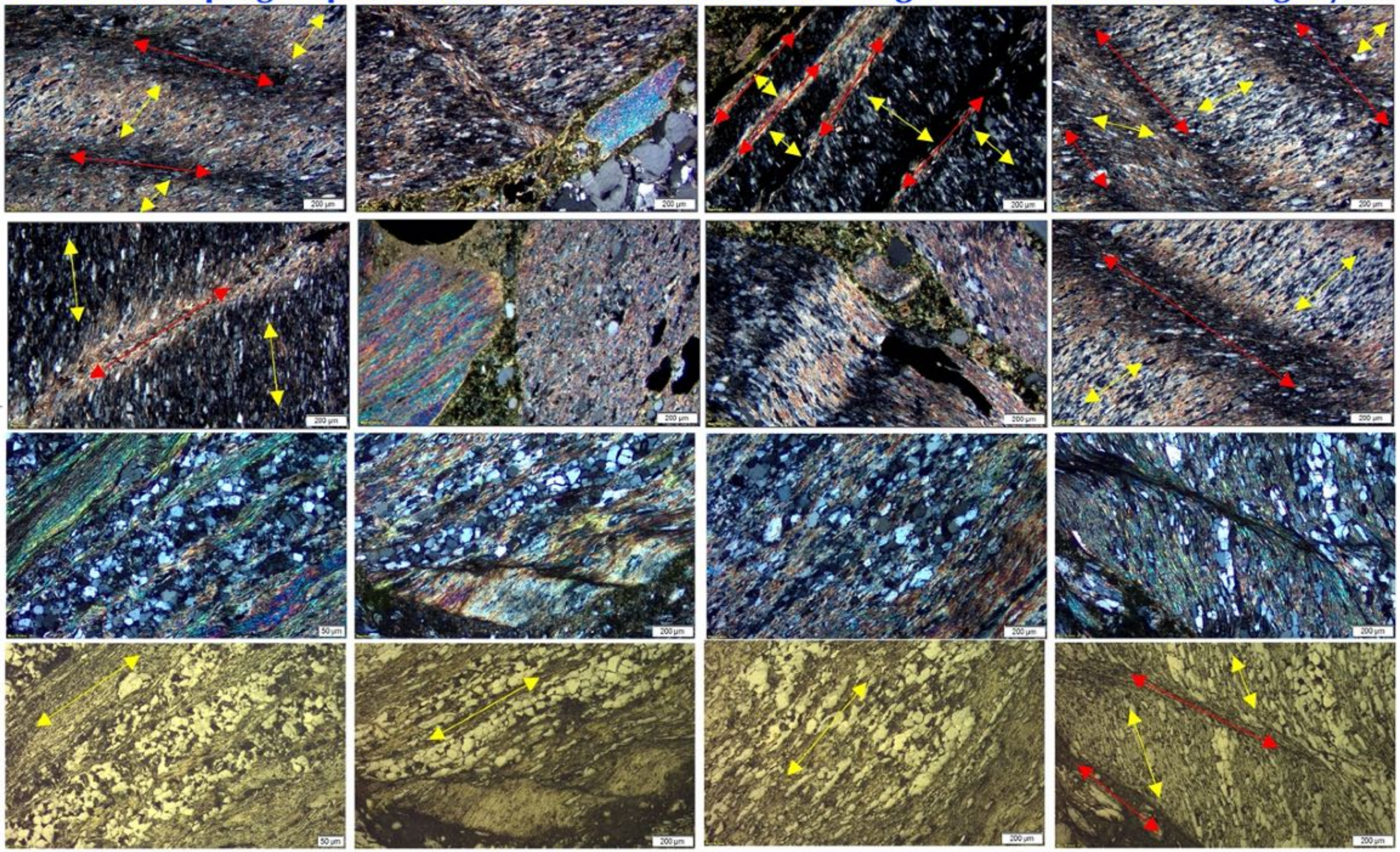
Increased fraction of abraded phyllite in mortar

↓

Increased Water Demand and Water Absorption

Phyllite

Phyllite - Mica Schist



- Phyllite is the most abundant aggregate, around 80% by volume, which are noticeably finer-grained than mica schist or quartzite and shows foliation planes, and folded/crenulation cleavages - from two-stage deformation of shale/mudstone by grinding actions of mother Earth during Grenvillian Orogeny.
- Fine grain size of muscovite, chlorite, and quartz grains in phyllite and the internal planes of weakness (cleavages and folded/crenulation cleavages) make phyllite highly susceptible to flaking, expansion from moisture absorption, which can aggravate during exposures to subfreezing temperatures.
- The texture of phyllite makes it more unsuitable for use as concrete aggregate than the mineralogy.

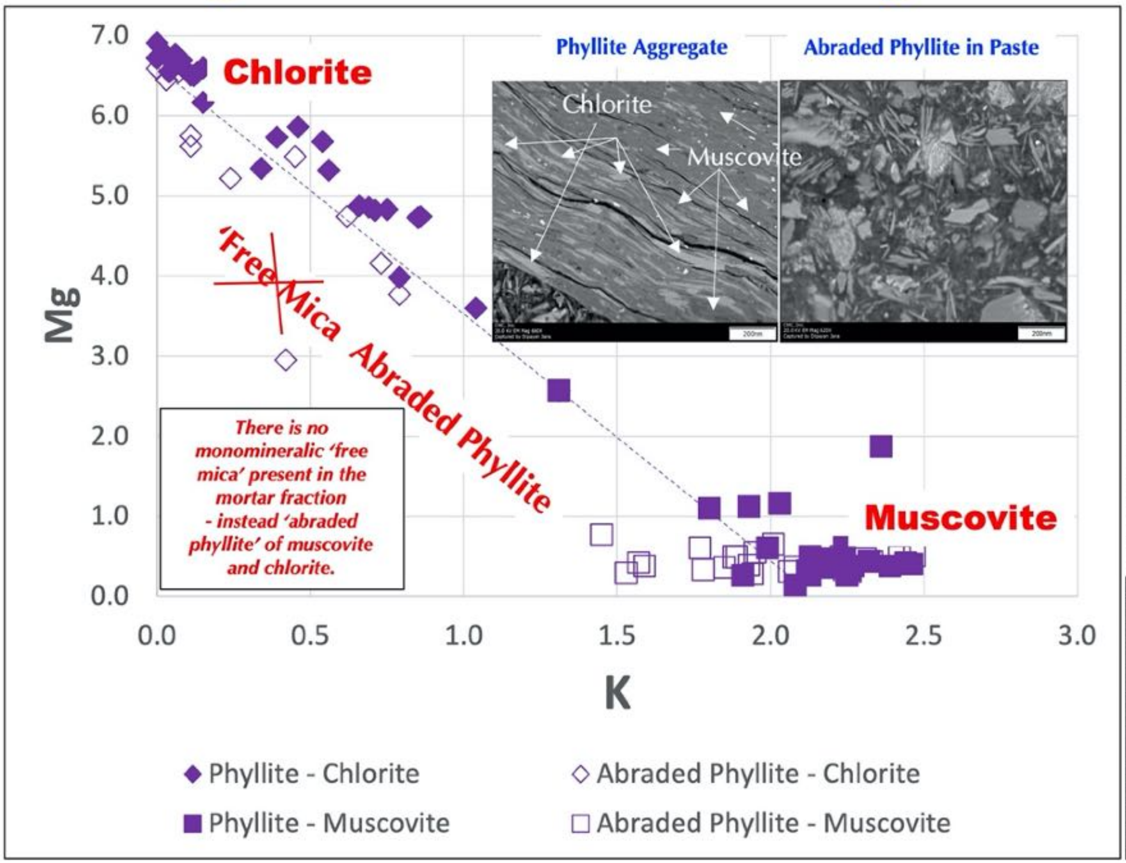
More than 80% of houses at ***high-risk*** *contained* ***phyllite*** *(Brough et al. 2023)*

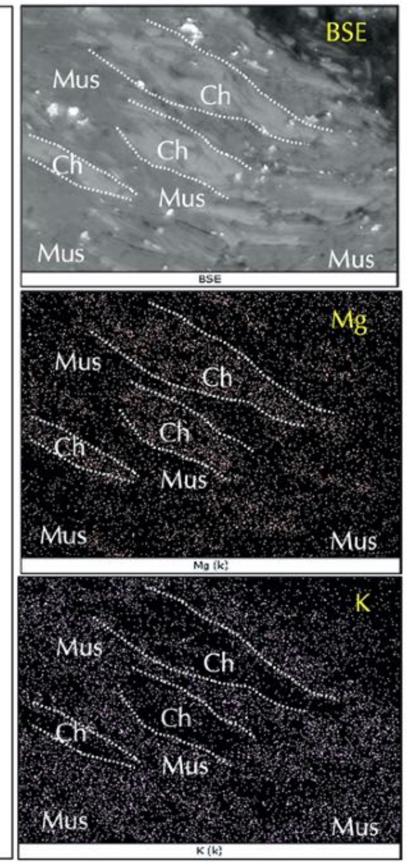
Transmitted (XPL) and Reflected-light micrographs of polished thin sections of defective blocks

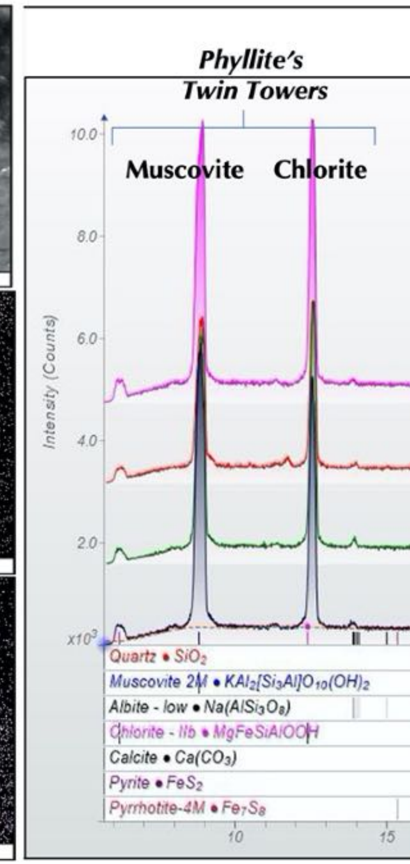
It is NOT Free Mica but Juxtaposed Layers of Intimately Mixed Mica and Chlorite

1

Mg-K SEM-EDS Plot   BSE Image   Mg-K Elemental Map   XRD







Phyllite (Pyrrhotite) Action Group **would have been the right group to form instead of** ***Mica Action Group!***

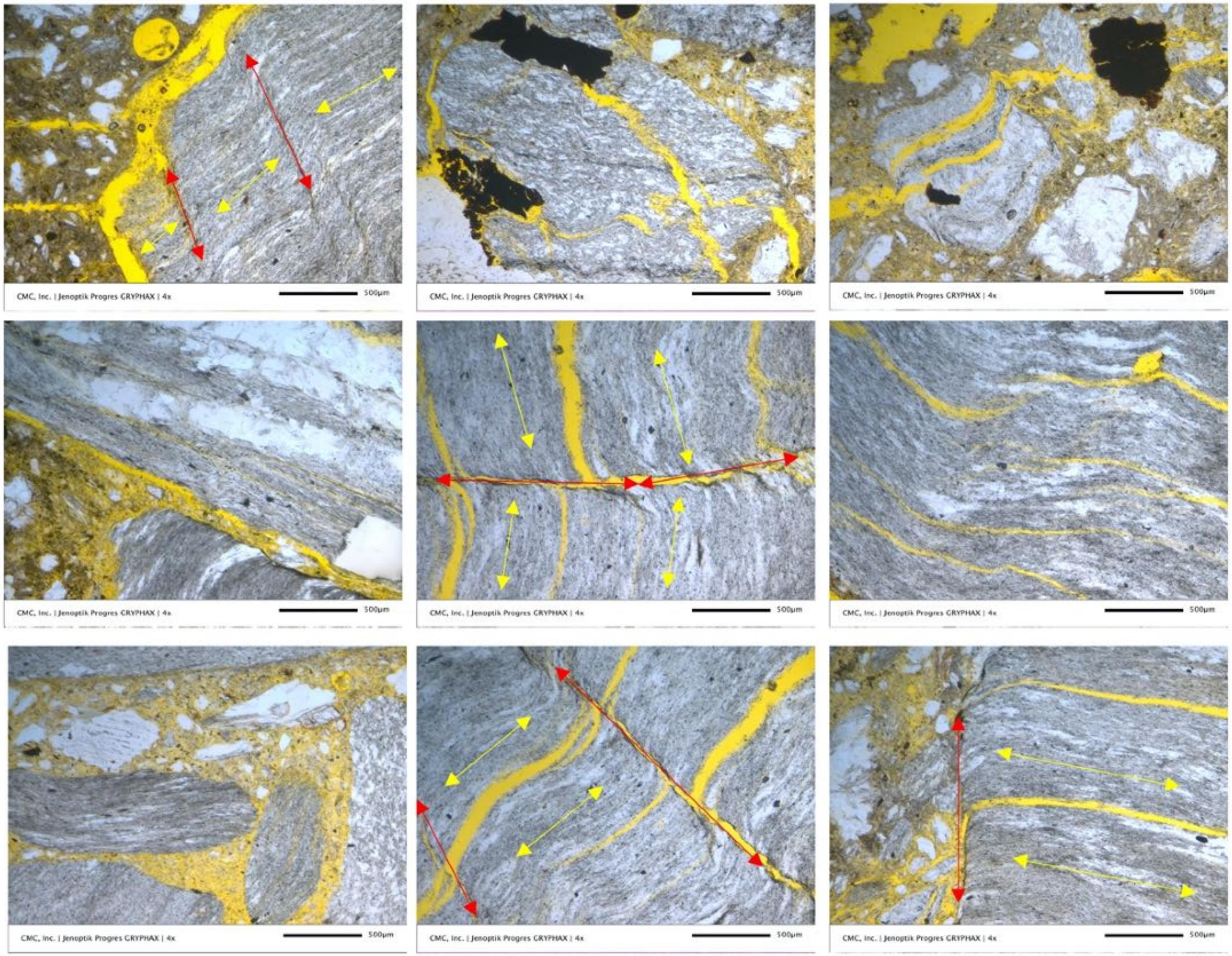
Backscatter electron image, Elemental Maps, and EDS Analyses of Phyllite in Aggregate and Abraded Phyllite in Mortar Fraction of Defective Blocks

Textural Microcracks in Phyllite - Along Foliation Planes & Crenulation Cleavage Planes

In and around Phyllite Grains Highlighted by Fluorescent Epoxy

2

Excellent Pathways for Penetration of Moisture and O_2 to Pyrrhotite

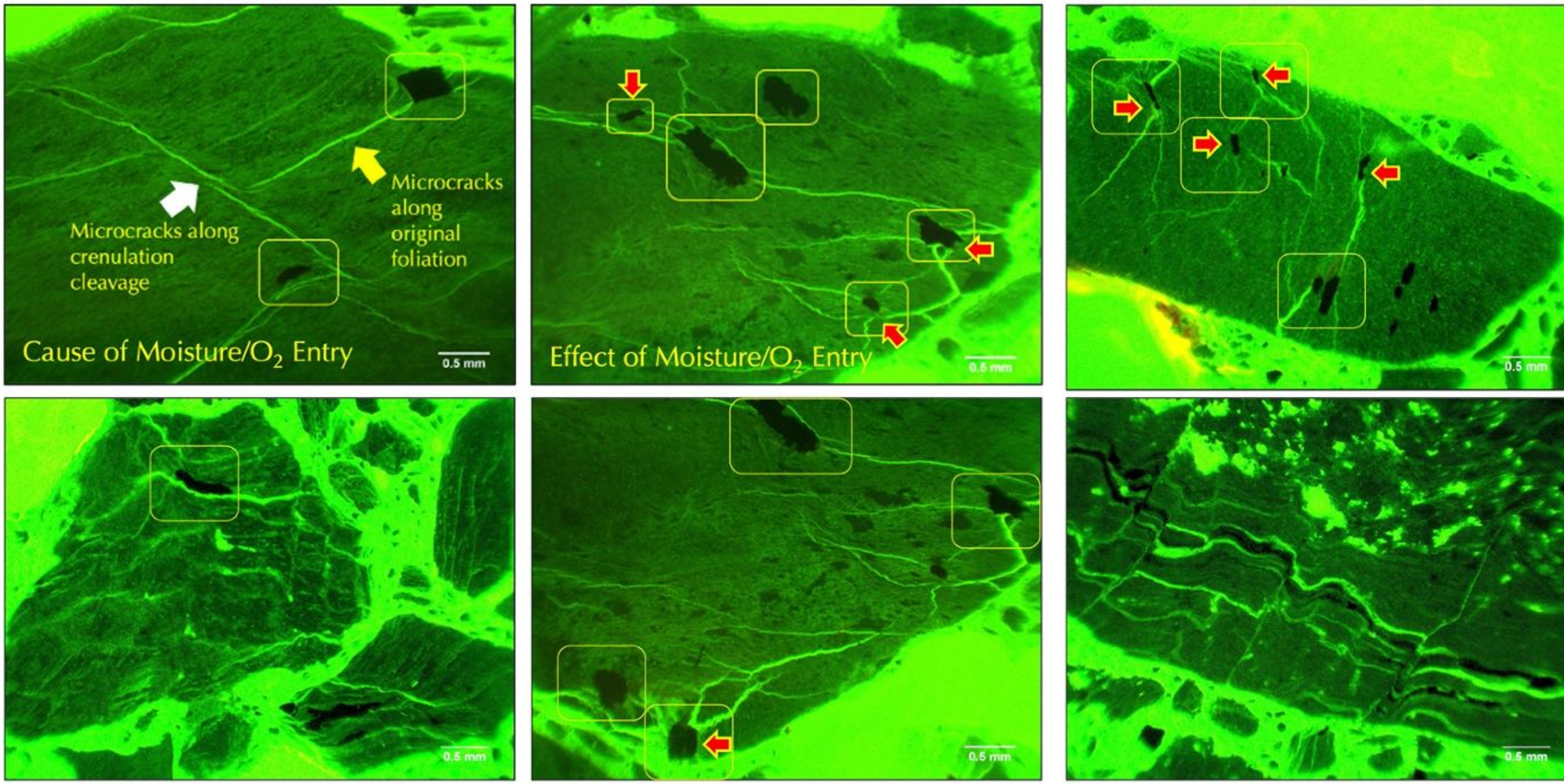


Transmitted light (PPL) micrographs of polished thin sections of defective blocks

Two Types of Microcracks in Phyllite

3

Inherent Textural Microcracks Following Foliation Planes & Crenulation Cleavage Planes
& Radial Microcracks from Oxidized Pyrrhotite Grains



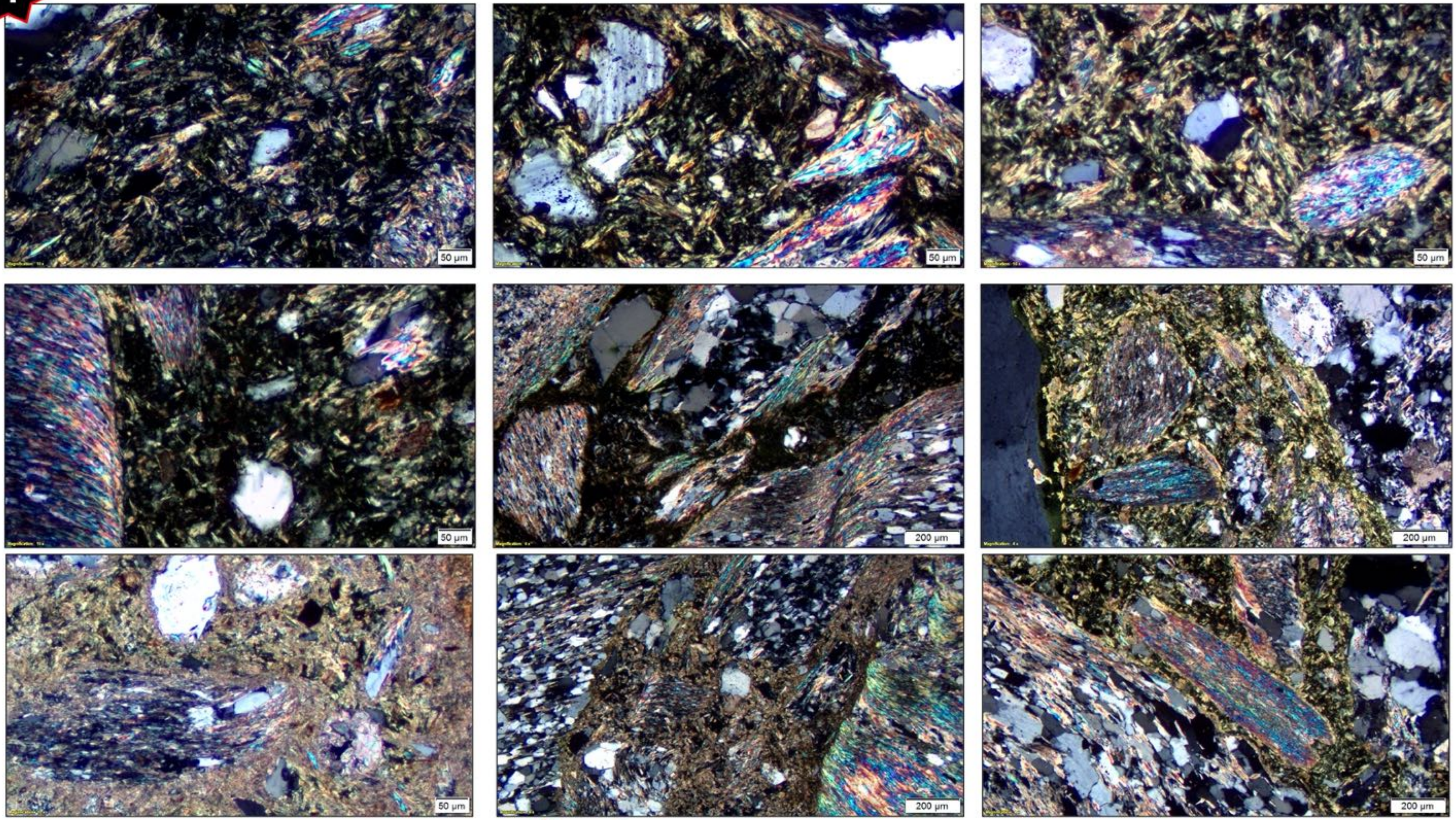
Both Types of Microcracks are responsible for Abundant Abraded Phyllite in Mortar Fraction

Micrographs of fluorescent dye-mixed epoxy-impregnated thin sections of defective blocks

Abundant Abraded Phyllite in Mortar Fraction (up to 50% by volume of mortar)

4

Phyllite Action Group would have been the right group to form than Mica Action Group!

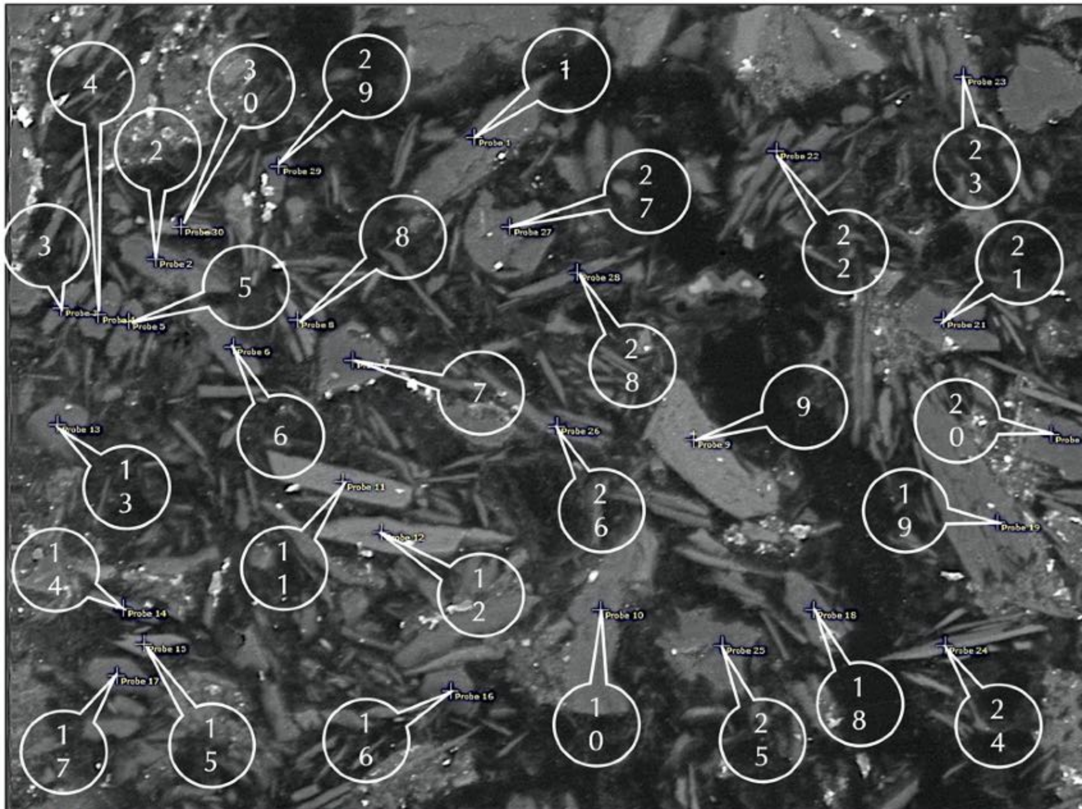


~~'Free Mica'~~ Abraded Phyllite

Transmitted-light (XPL) micrographs of polished thin sections of defective blocks

4 Abundant Abraded Phyllite in Mortar Fraction (up to 50% by volume of mortar)

Phyllite Action Group would have been the right group to form than Mica Action Group!



Atomic Weight Percent of:

Probes	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Phase
1	**62.81**	0.64	0.49	**12.35**	**20.83**	0.00	**2.23**	0.56	0.06	0.03	Muscovite
2	**62.69**	0.70	0.47	**12.59**	**20.51**	0.00	**2.31**	0.56	0.07	0.11	Muscovite
3	**62.72**	0.61	0.49	**12.62**	**20.61**	0.00	**2.42**	0.46	0.04	0.04	Muscovite
4	**62.51**	**6.03**	0.00	**6.68**	**24.71**	0.00	0.05	0.02	0.00	0.00	Muscovite
5	**62.50**	**6.00**	0.00	**6.86**	**24.58**	0.00	0.04	0.02	0.00	0.00	Muscovite
6	**62.73**	0.69	0.31	**13.07**	**20.30**	0.00	**2.26**	0.42	0.11	0.10	Muscovite
7	**66.57**	0.19	0.00	0.00	**33.23**	0.00	0.00	0.00	0.00	0.00	Quartz
8	**61.71**	0.20	**6.59**	**11.70**	**17.63**	0.00	0.00	0.59	0.03	**1.54**	Chlorite
9	**61.73**	0.09	**6.45**	**12.73**	**17.15**	0.00	0.03	0.01	0.00	**1.81**	Chlorite
10	**63.08**	0.34	**2.95**	**6.70**	**23.19**	0.00	0.42	**3.02**	0.00	0.30	Paste
11	**61.60**	0.03	**6.55**	**12.87**	**16.82**	0.00	0.07	0.04	0.00	**2.00**	Chlorite
12	**61.83**	0.24	**5.49**	**12.43**	**17.73**	0.00	0.45	0.12	0.05	**1.65**	Chlorite
13	**62.86**	0.66	0.55	**11.97**	**21.02**	0.00	**1.95**	0.88	0.02	0.08	Muscovite
14	**62.53**	**5.68**	0.00	**7.18**	**24.34**	0.00	0.06	0.16	0.00	0.04	Muscovite
15	**61.99**	0.19	**5.75**	**11.75**	**18.19**	0.00	0.11	0.45	0.05	**1.52**	Chlorite
16	**62.90**	0.70	0.49	**11.22**	**21.39**	0.00	**1.89**	1.21	0.09	0.10	Muscovite
17	**63.34**	0.53	**1.74**	**8.18**	**23.16**	0.00	0.66	**2.04**	0.02	0.34	Paste
18	**61.55**	0.28	**7.31**	**6.59**	**19.98**	0.00	0.33	3.19	0.12	**0.63**	Chlorite
19	**63.46**	0.66	0.36	**9.90**	**23.17**	0.00	**1.85**	0.43	0.06	0.12	Muscovite
20	**66.56**	0.19	0.00	0.00	**33.19**	0.00	0.00	0.02	0.01	0.03	Quartz
21	**62.47**	**6.08**	0.00	**6.86**	**24.53**	0.00	0.02	0.01	0.03	0.00	Muscovite
22	**62.77**	0.77	0.37	**12.29**	**20.77**	0.00	**2.08**	0.81	0.05	0.08	Muscovite
23	**62.85**	0.84	0.28	**12.41**	**20.77**	0.00	**1.94**	0.79	0.11	0.02	Muscovite
24	**62.27**	0.58	**3.77**	**11.71**	**19.29**	0.00	0.79	0.64	0.08	**0.88**	Chlorite
25	**66.44**	0.21	0.00	0.73	**32.61**	0.00	0.00	0.00	0.00	0.00	Quartz
26	**62.98**	0.66	0.39	**11.56**	**21.36**	0.00	**1.93**	0.89	0.10	0.14	Muscovite
27	**63.02**	1.56	0.29	**11.05**	**21.58**	0.00	**1.53**	0.36	0.48	0.13	Muscovite
28	**62.93**	0.66	0.65	**11.56**	**21.28**	0.00	**1.81**	0.94	0.04	0.12	Muscovite
29	**62.56**	**5.61**	0.00	**6.89**	**24.56**	0.00	0.19	0.15	0.01	0.02	Muscovite
30	**62.25**	0.20	**4.16**	**11.82**	**19.04**	0.00	0.73	0.56	0.01	**1.24**	Chlorite

Brighter flakes are Chlorite and darker flakes are Muscovite

~~'Free Mica'~~ Abraded Phyllite

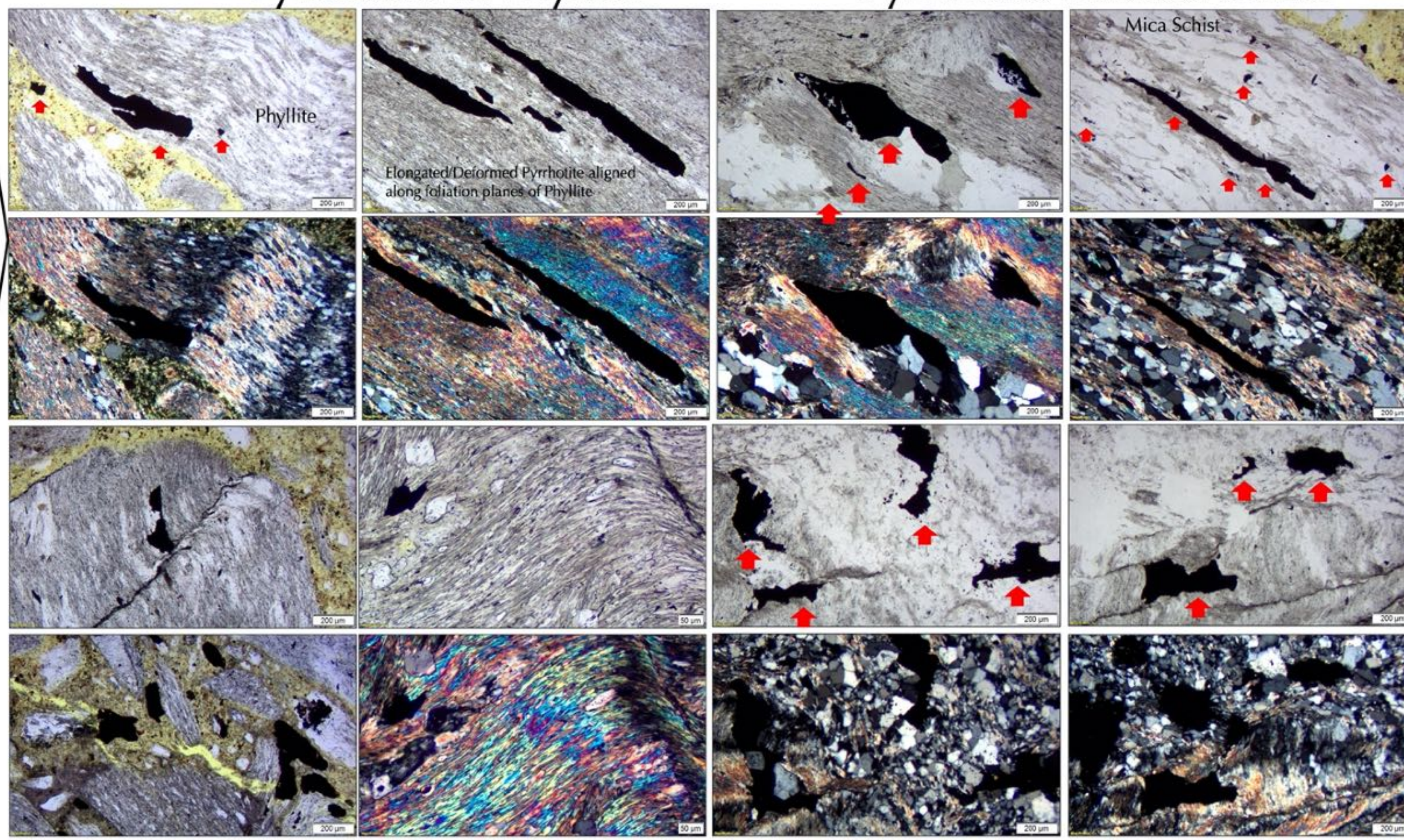
Backscatter Electron Image (Left) and X-ray Microanalysis (Right) of Phyllite in Mortar Fraction in Block from House 1

3rd Culprit - Pyrrhotite & Other Iron Sulfides - The Cancel Cell!

1. Finely disseminated pyrrhotite and pyrite in phyllite for oxidation
2. Expansion
3. Radial microcracks
4. Crumbling of phyllite
5. Sulfate release for ISA in paste

Extensive Cracking & Crumbling of Blocks

Pyrrhotite in Phyllite **Pyrrhotite in Mica Schist**



Along Foliation/Schistosity

Isolated, Disseminated

Pyrrhotite Action Group **would have been the right group to form than** ***Mica Action Group*****!**

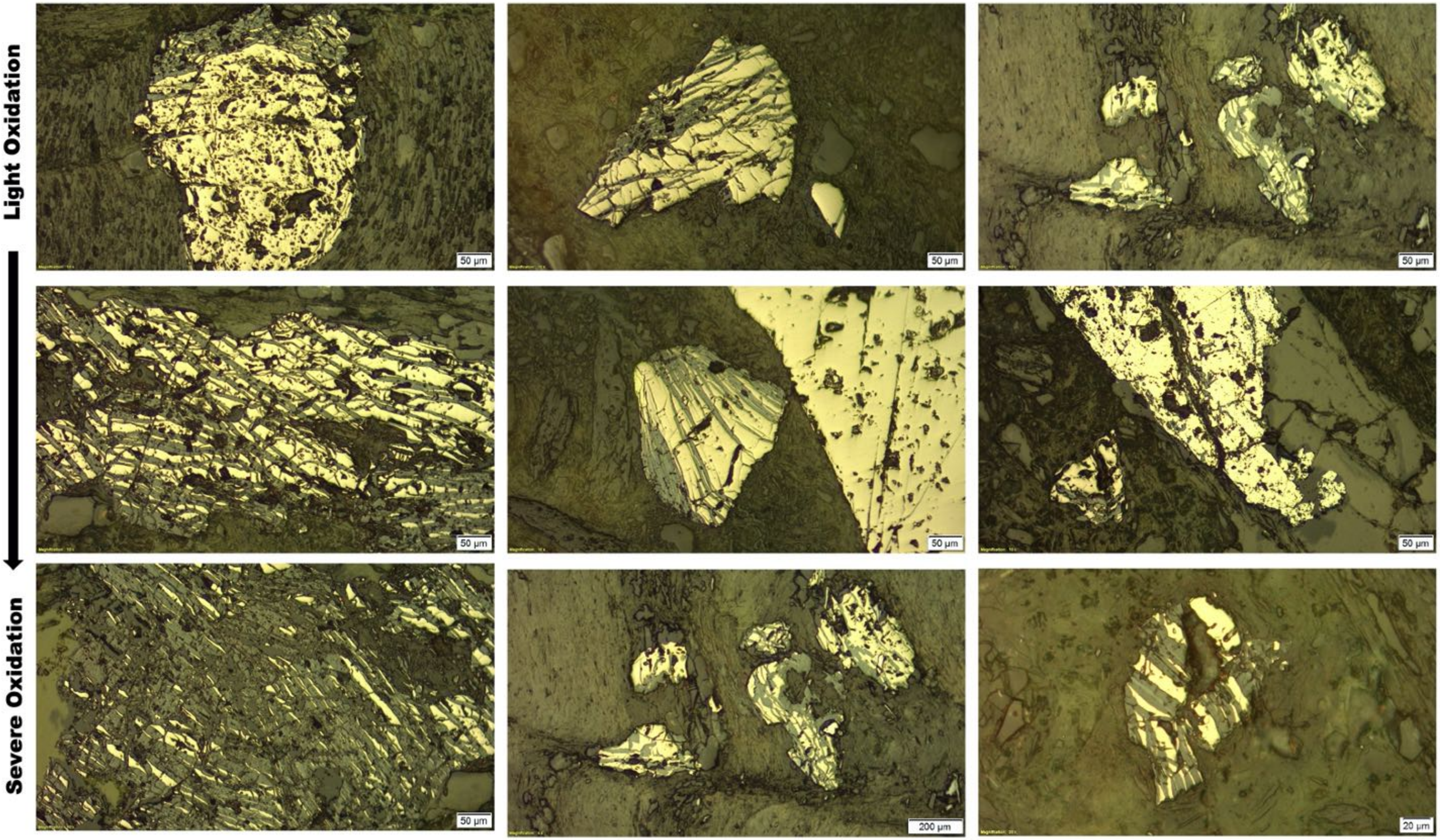
www.cmc-concrete.com

Disseminated & Elongated/Deformed Pyrrhotite Grains in Phyllite and Mica Schist Aggregates Aligned along the Plane of Foliation in Phyllite or Schistosity in Schist

www.petrography.net

Ore Microscopy - Best Method to Detect Oxidized Pyrrhotite in Defective Blocks

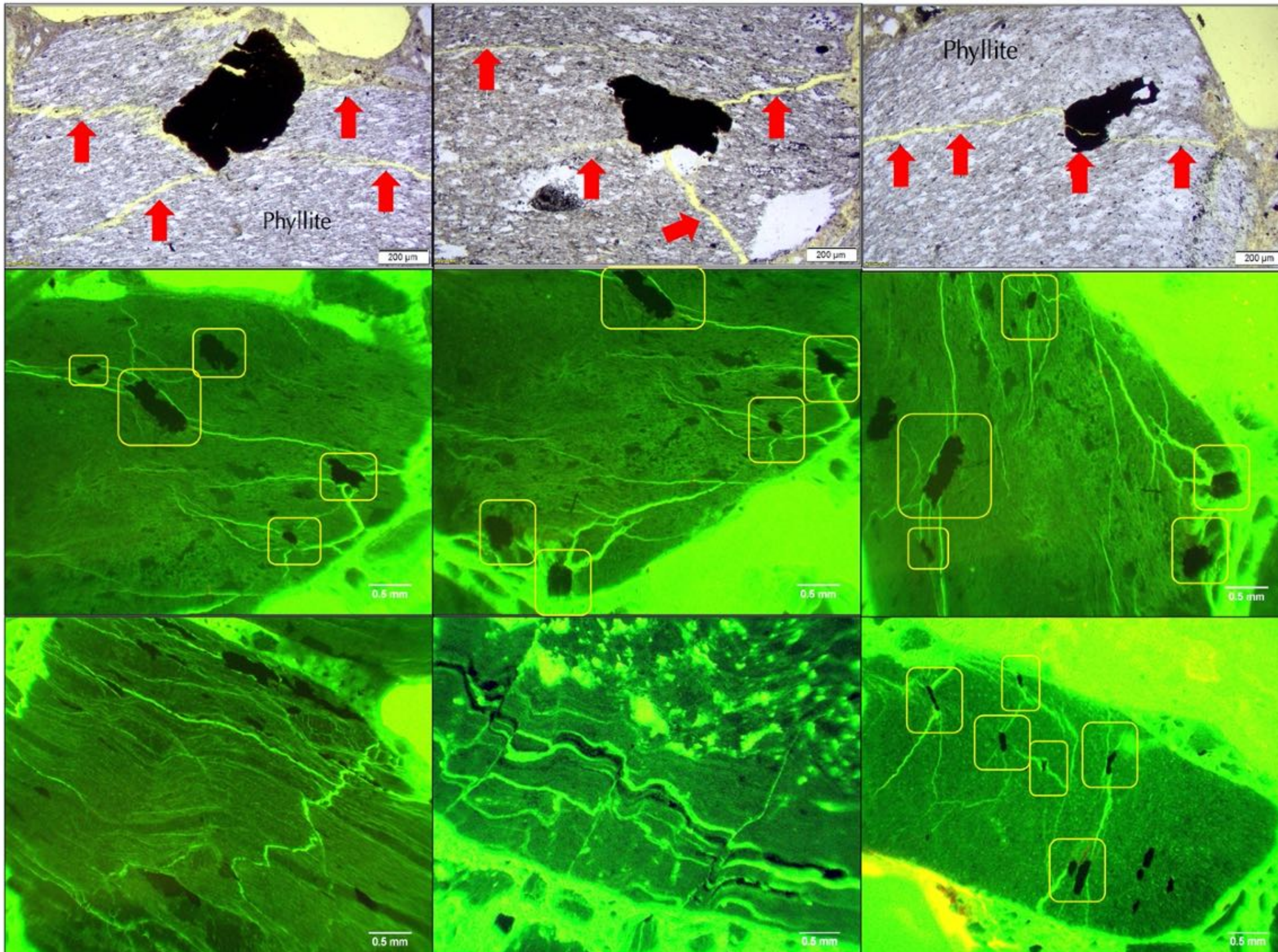
Characteristic 'Striated' Appearance of Dark Fe-O Bands in Bright Fe-S Matrix of Oxidized Pyrrhotite



Reflected-light micrographs of polished thin sections of defective blocks

Fluorescent Microscopy - Best Method to Detect Radial Microcracks

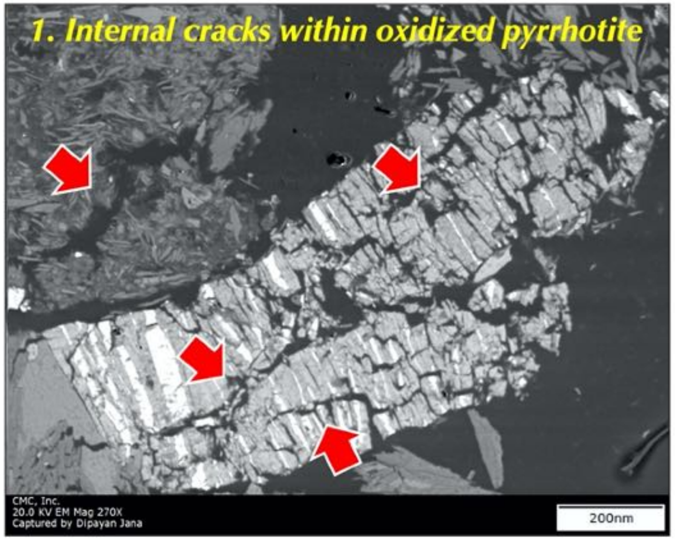
Radial Microcracks - Result of Expansion from Pyrrhotite Oxidation

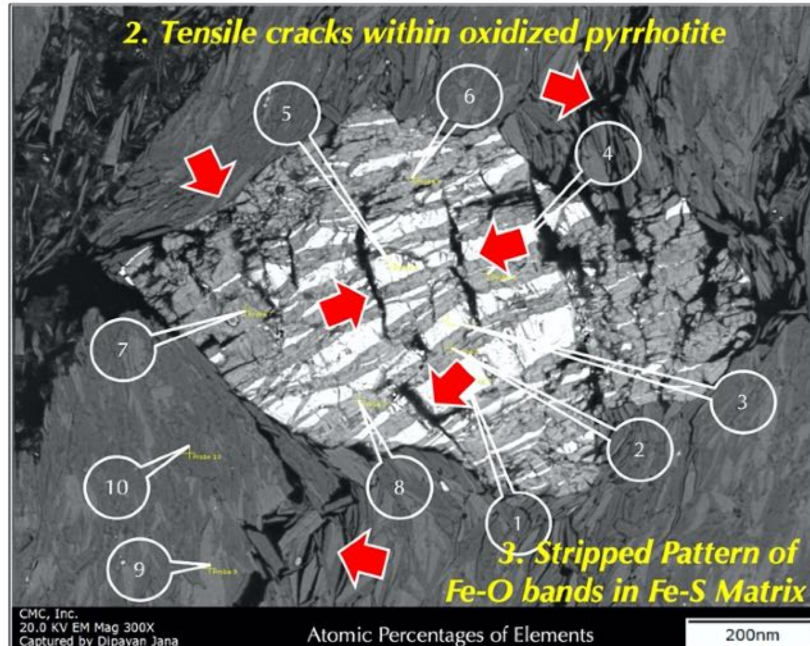


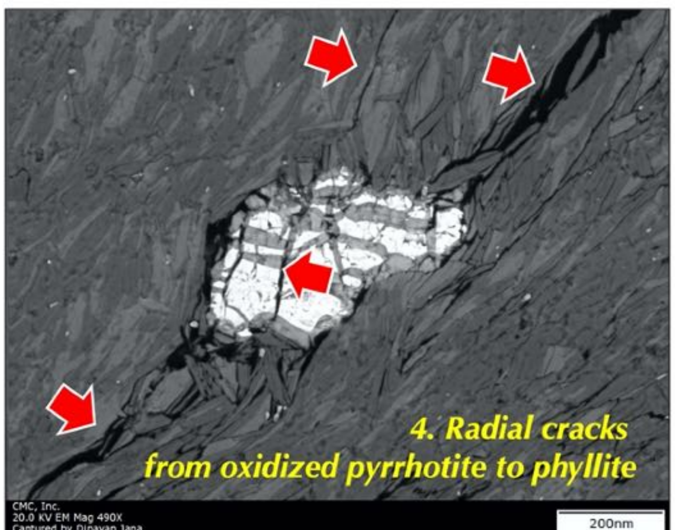
Transmitted (PPL) and UV-light micrographs of polished thin sections of defective blocks

BSE Imaging - Best Method for Detecting Expansion from Pyrrhotite Oxidation

Microcracks Within & Around Oxidized Pyrrhotite Depicting Striated Patterns of Fe-O Bands in Fe-S Matrix







SEM-EDS Analyses of Fe-O and Fe-S Bands

Atomic Percentages of Elements

Probe	Phase	O	Ca	Si	Al	Na	Mg	S	K	Ti	Fe
1	Pyrrhotite	5.79	0.00	0.54	0.00	0.00	0.00	**59.63**	0.07	0.00	**33.55**
2	Oxidized Pyrrhotite	**40.06**	0.86	12.87	0.00	0.00	0.00	7.54	0.10	0.00	**37.77**
3	Pyrrhotite	4.96	0.00	0.46	0.00	0.00	0.00	**60.40**	0.10	0.00	**33.77**
4	Oxidized Pyrrhotite	**47.42**	0.89	12.01	0.00	0.00	0.00	10.40	0.00	0.00	**28.88**
5	Pyrrhotite	4.6	0.00	0.24	0.00	0.00	0.00	**60.49**	0.00	0.00	**34.21**
6	Oxidized Pyrrhotite	**45.15**	0.94	11.63	0.02	0.00	0.00	4.59	0.02	0.00	**36.98**
7	Oxidized Pyrrhotite	**49.16**	1.15	15.11	0.00	0.00	0.00	9.05	0.00	0.04	**24.92**
8	Oxidized Pyrrhotite	**46.38**	0.95	12.44	0.61	0.00	0.00	6.79	0.00	0.00	**32.37**
9	Chlorite	**50.42**	0.02	**17.37**	**15.57**	0.00	**8.62**	0.14	0.04	0.04	**7.60**
10	??	**50.67**	1.39	**14.58**	0.00	0.00	0.00	8.10	0.05	0.00	24.60

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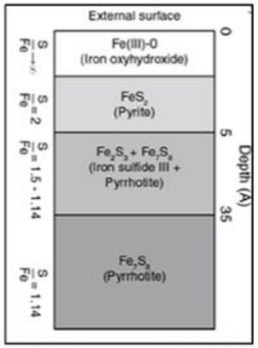
Backscatter electron images and SEM-EDS analyses of oxidized pyrrhotite grains in host phyllite

S/Fe vs. O/Fe Atomic Plots - Oxidized Pyrrhotite from Ireland and Connecticut

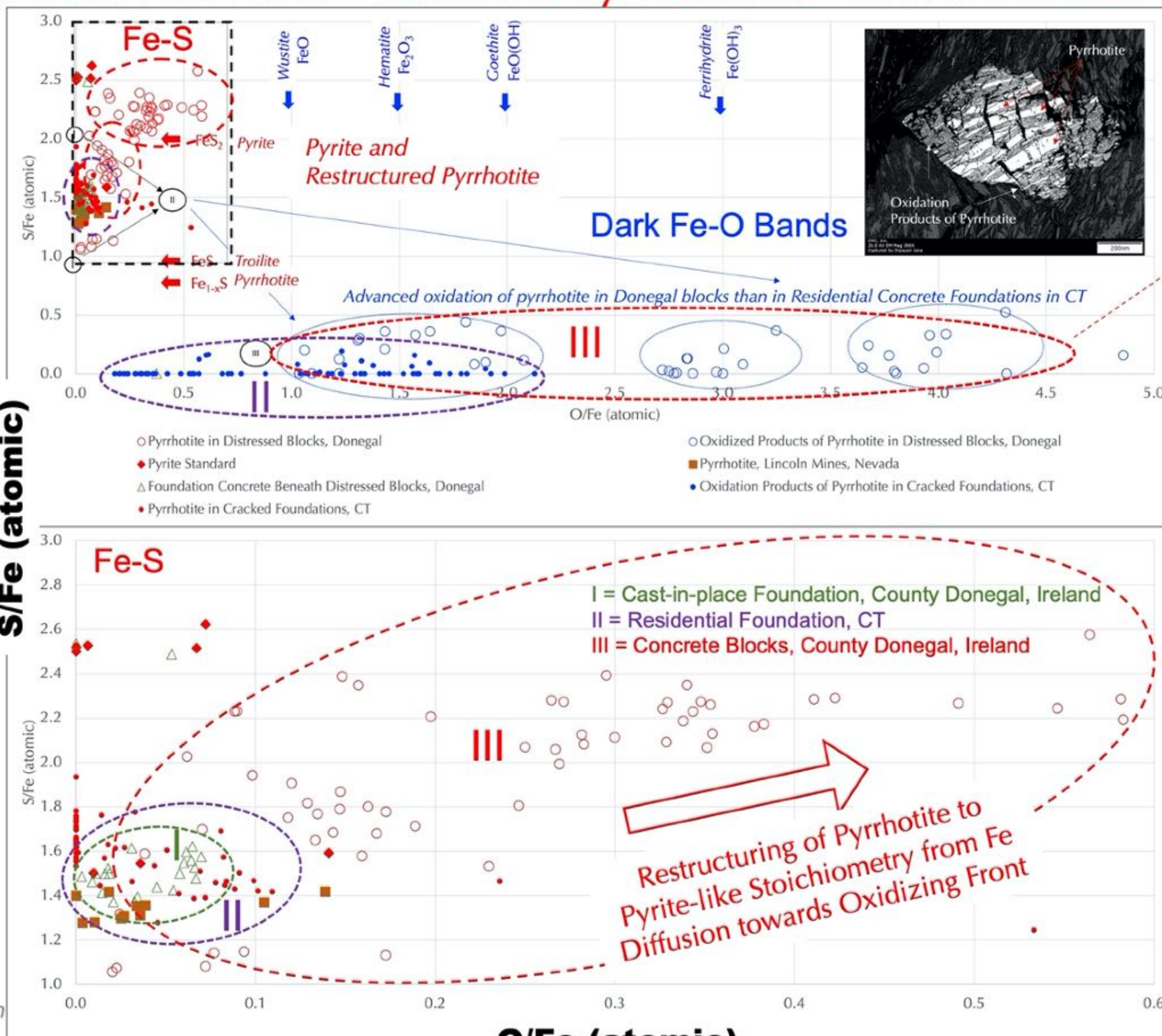


Oliveira et al. (2014)

O/Fe atomic ratios in oxidation bands of oxidized pyrrhotite grains in Donegal blocks are noticeably higher

than

O/Fe ratios of oxidized pyrrhotite in Connecticut



S/Fe vs. O/Fe atomic ratios of oxidized pyrrhotite grains in defective blocks

Advanced Oxidation of Iron Sulfide in Ireland from:

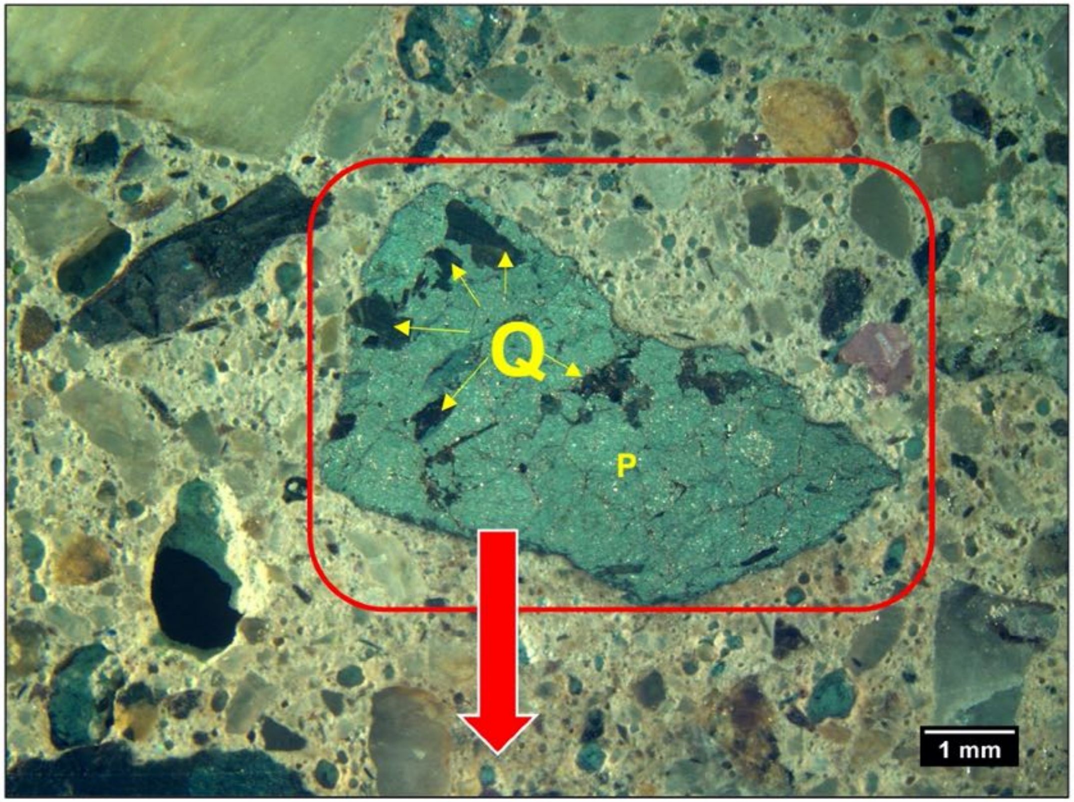
1. **Open microstructure of blocks**
2. **Phyllite host**
3. **Fine disseminated grain size of pyrrhotite**

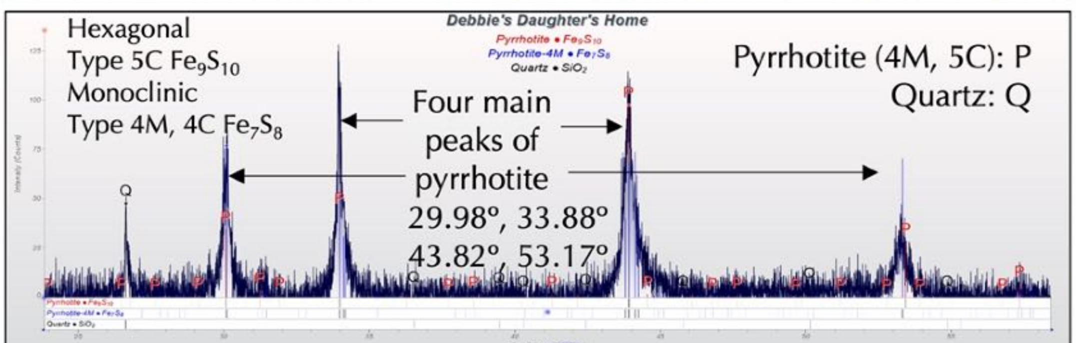
No oxidized bands in pyrrhotite in cast-in-place foundation

Most oxidized pyrrhotite grains in blocks are from mortar fractions in blocks

In CT - Coarse Pyrrhotite Grains Allowed Direct In-Situ XRD by Micro-Drilling

Typical 'Temple Pattern' of Pyrrhotite

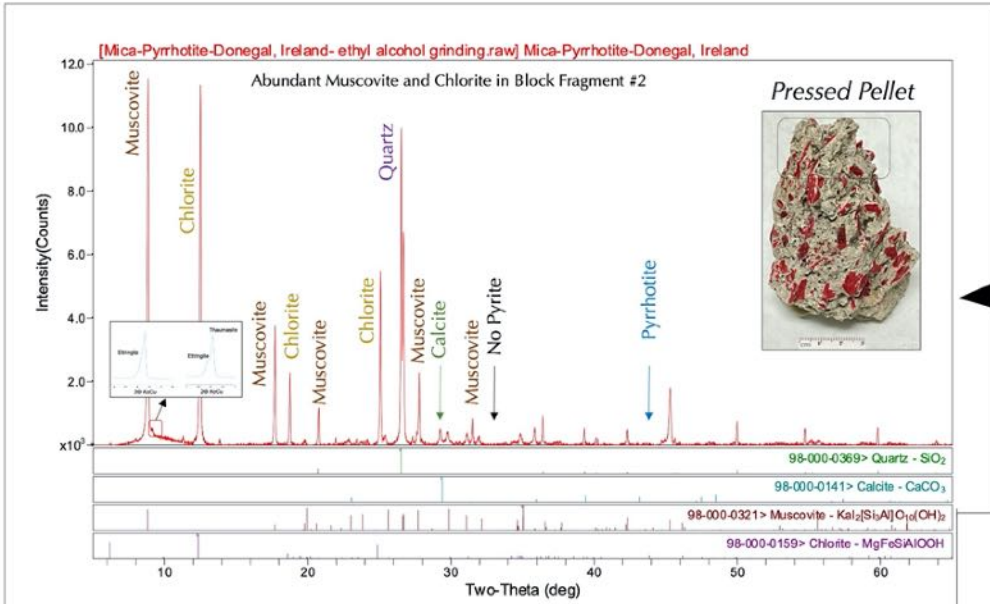




Drilled directly with a micro-drill and dust analyzed on zero-background silicon wafer

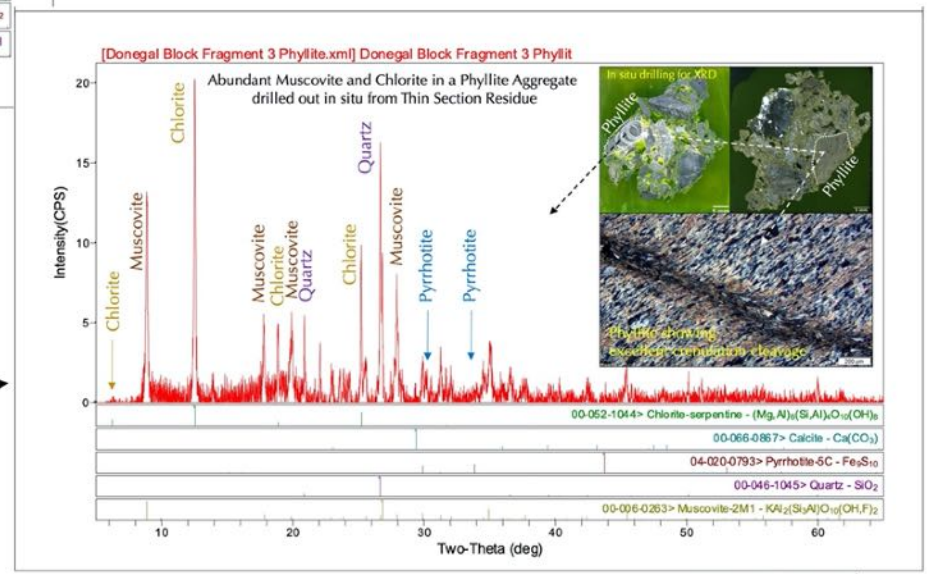
Pyrrhotite dust collected by direct in situ micro drilling a grain and spread across a zero background silicon wafer sample holder over a thin film of petroleum jelly for XRD analysis at a slow scan rate

But In Ireland - Due to Finely Disseminated Forms, Direct XRD of Pyrrhotite is Difficult



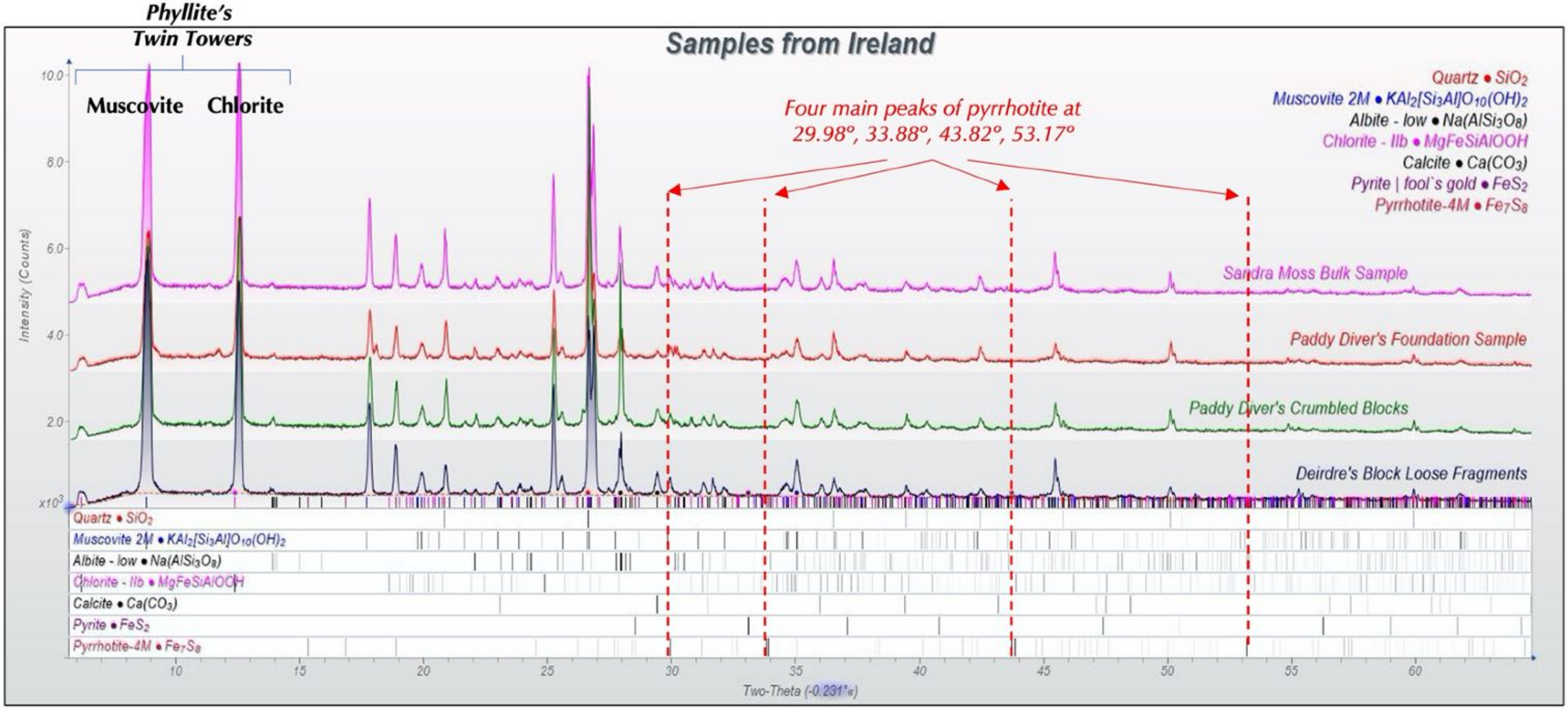
Bulk XRD of Blocks cannot find Pyrrhotite

In-Situ XRD of Phyllite can find Pyrrhotite



Powder finer than 44-micron from bulk sample was side-loaded in a sample holder (not pressed) for XRD whereas an aggregate grain was analyzed directly with some dust collected by drilling

XRD Patterns of Distressed Blocks from Three Homes and One Sound Foundation Showed Mineralogical Similarities from Abundant Phyllite Aggregate in All

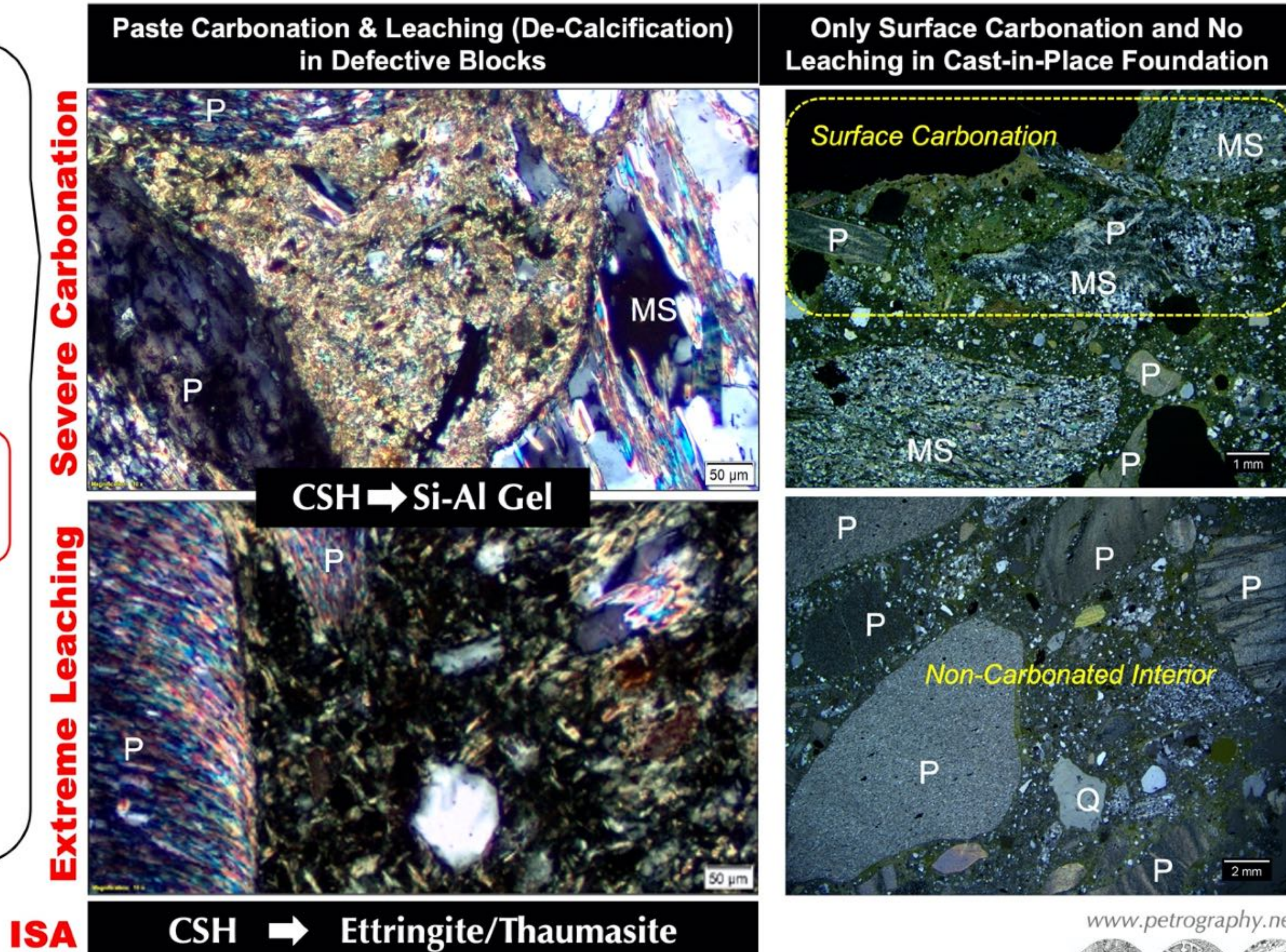


4th Culprit - Paste - The Sulfate/Carbonate Contaminated Blood!

1. Yes, it is Low volume (< 10%)
2. But, it is Loaded with abraded phyllite and sulfate
3. ***ISA***
4. ***Leaching***
5. ***Carbonation***

⬇

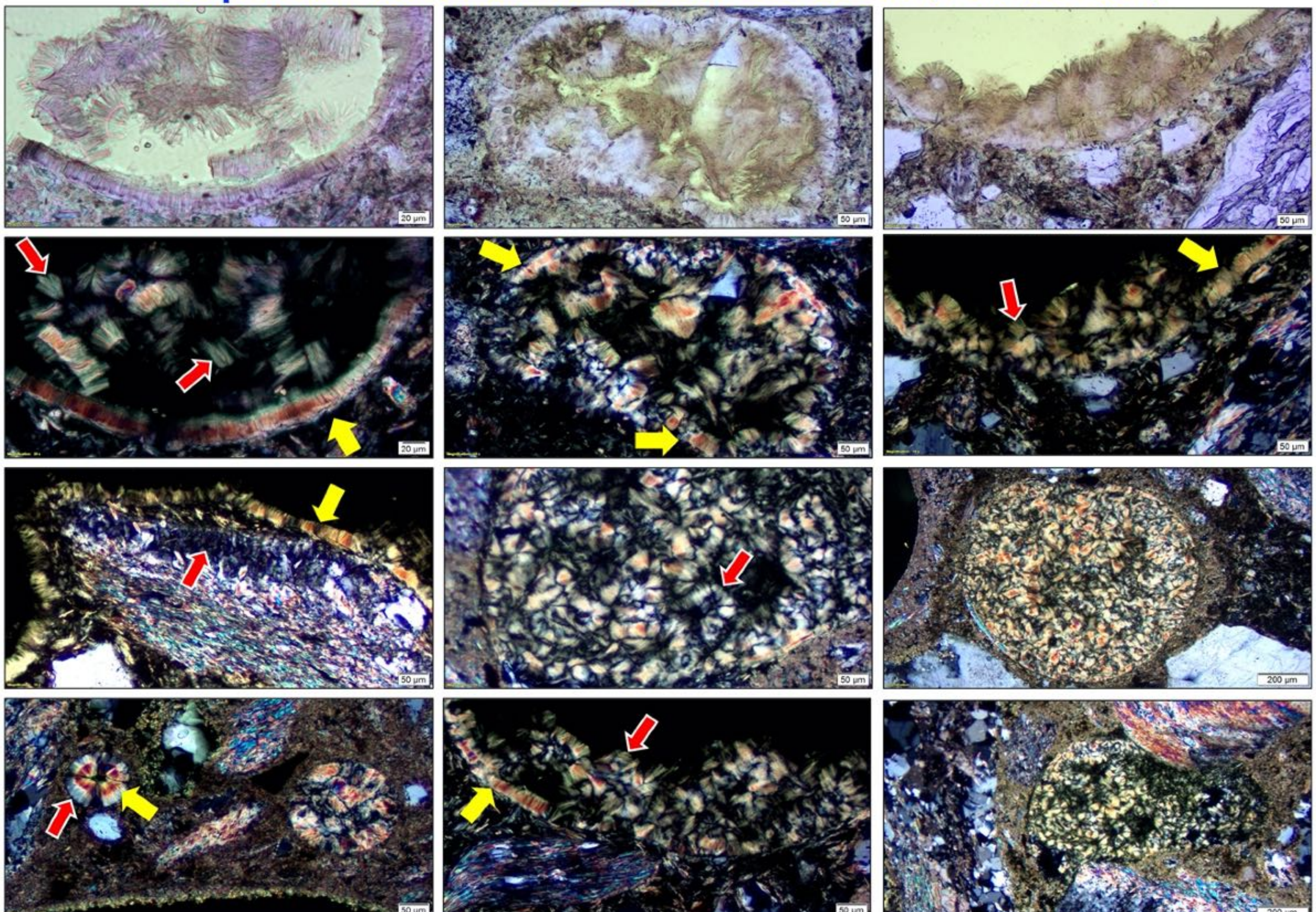
Large-scale Crumbling of Blocks



Micrographs of thin sections of defective blocks (left) and cast-in-place foundation (right)

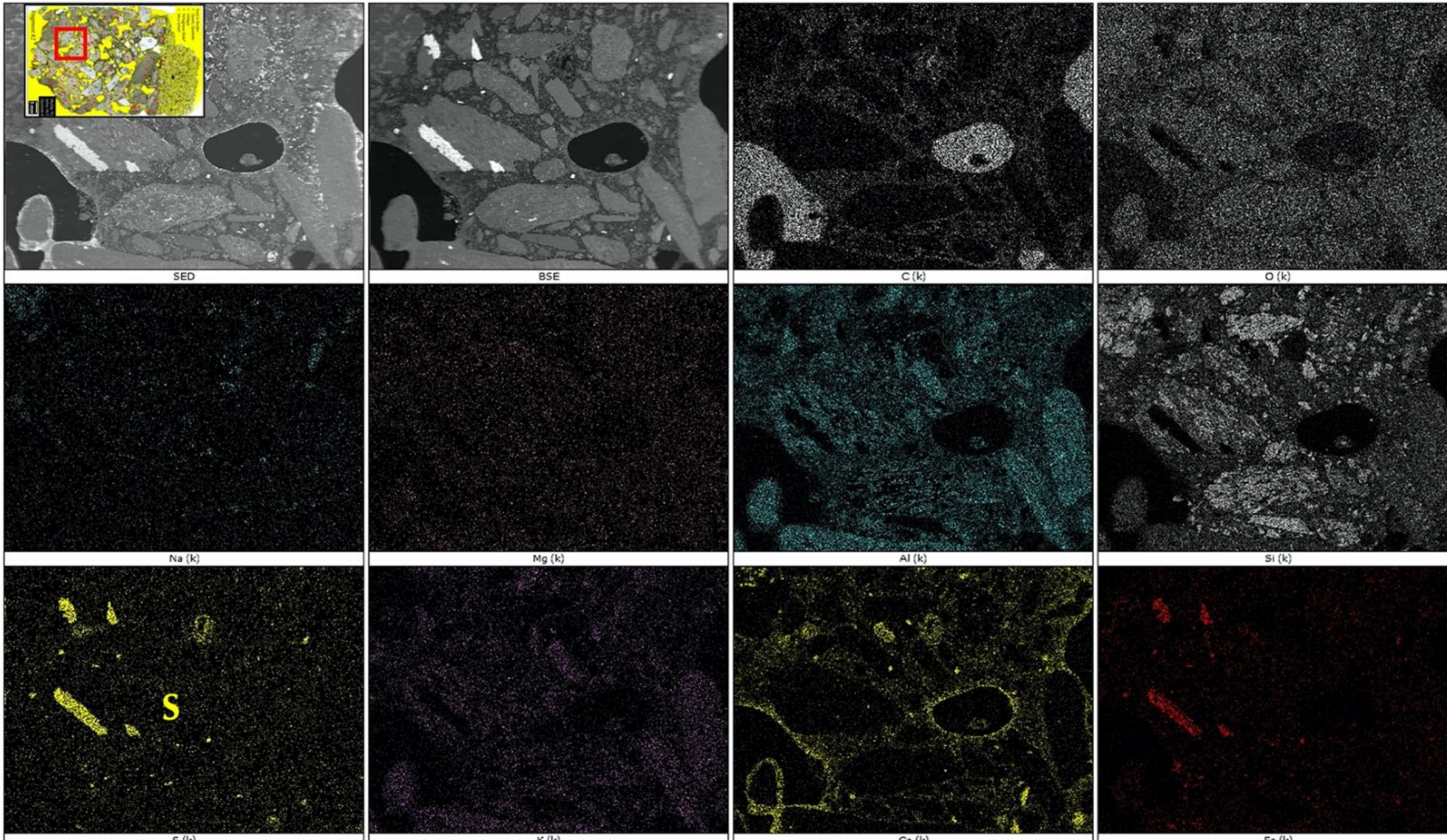
Telltale Signs of ISA - Profuse Secondary Ettringite and Thaumasite in Voids and Pore Spaces

Precipitated Products of Internal Sulfate Attacks (E-ISA & T-ISA)



Plane and Corresponding Cross Polarized Light Images from a Petrographic Microscope

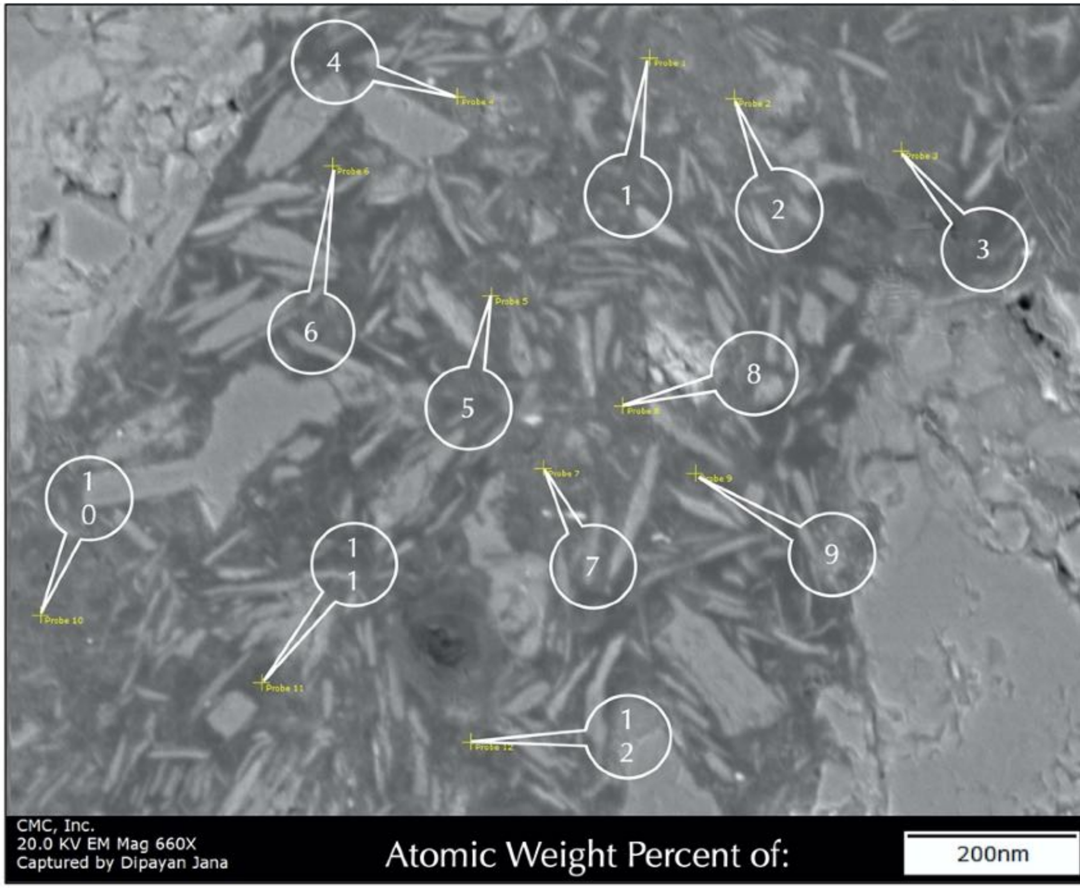
In Search of ISA - Scavenged Entire Thin section for S-rich areas in Elemental Mapping



Scavenging a thin section through rasters of elemental maps for S, Ca, Si, Al, Mag, Na, C, O

SEM-EDS Analysis of Leached Paste of Si-Al Gel

(Notice Abundant Phyllite Flakes in Mortar)



Backscatter Electron Image

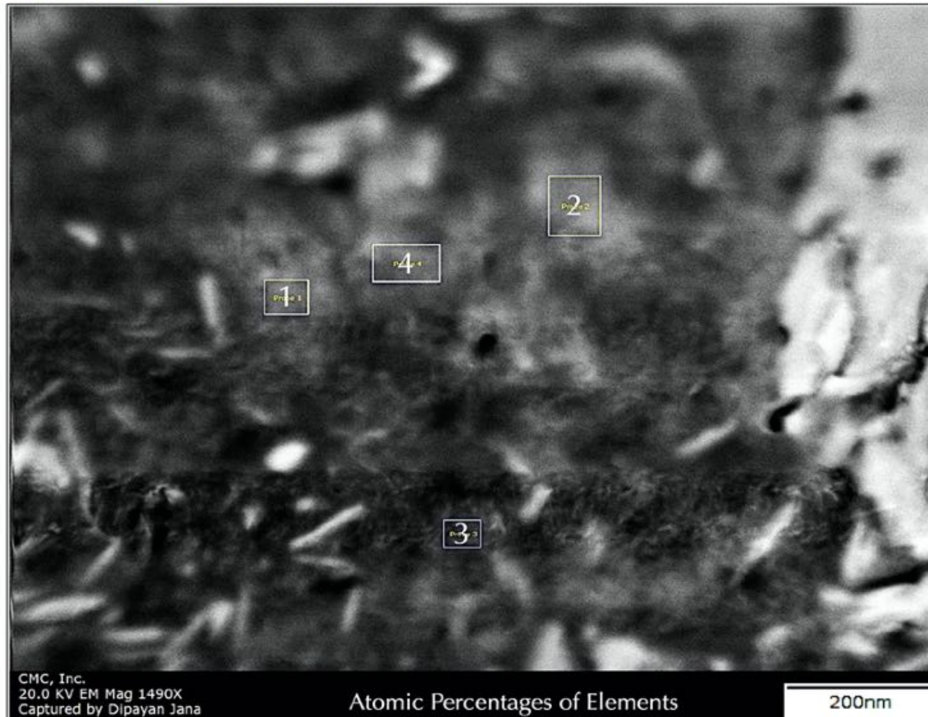
Probes	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Phase
1	53.05	1.78	2.11	7.31	30.49	0.00	0.16	4.06	0.29	0.74	Paste
2	50.62	1.95	1.03	7.55	32.79	0.00	0.17	4.70	0.30	0.91	Paste
3	50.19	0.51	1.13	8.08	33.24	0.00	0.44	5.67	0.00	0.74	Paste
4	54.72	0.88	0.61	7.12	22.53	0.00	0.77	12.74	0.15	0.48	Paste
5	55.30	0.44	1.05	8.38	26.21	0.00	0.70	6.74	0.08	1.10	Paste
6	60.46	0.52	1.07	7.68	24.95	0.00	0.47	4.08	0.15	0.61	Paste
7	54.78	0.61	1.58	7.11	24.24	0.00	0.27	10.17	0.18	1.05	Paste
8	55.01	0.62	0.79	8.35	27.89	0.00	0.70	6.03	0.02	0.60	Paste
9	49.87	0.74	0.55	12.58	31.21	0.00	2.01	2.30	0.11	0.63	Paste
10	49.89	0.93	1.04	18.70	24.88	0.00	3.58	0.21	0.07	0.69	Paste
11	50.54	0.33	4.13	10.35	28.38	0.00	1.04	3.40	0.09	1.73	Paste
12	56.51	0.49	0.43	6.57	26.65	0.00	0.18	6.32	2.44	0.42	Paste

SEM-EDS Analyses at the tips of Callouts

Si-Al Gel (No S)

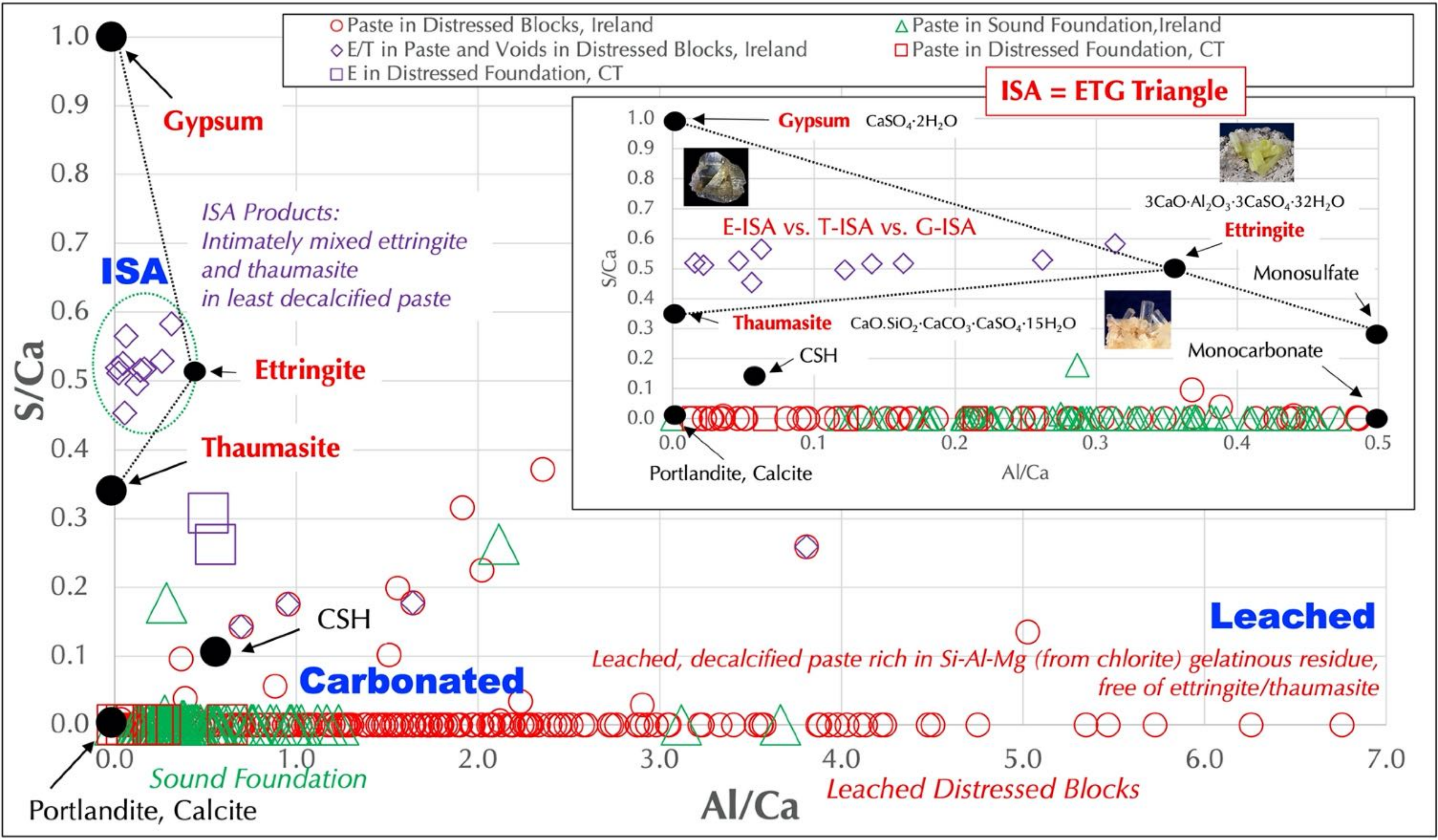
SEM-EDS Analysis of ISA-Affected S-Rich Regions in Paste

Probe	Phase	O	Ca	Si	Al	Na	Mg	S	K	Ti	Fe
1	Paste	**46.91**	**20.97**	**12.43**	5.49	0.00	1.47	**11.08**	0.14	0.13	1.04
2	Paste	**41.56**	**8.55**	**31.74**	**8.16**	0.00	**5.60**	1.50	0.66	0.10	1.82
3	Paste	**38.01**	2.22	**40.90**	**11.16**	**6.32**	0.02	0.30	0.68	0.06	0.25
4	Paste	**47.31**	**10.15**	**23.90**	**7.08**	0.43	**7.63**	1.45	0.14	0.15	1.46
5	Paste	**37.36**	**7.48**	**36.91**	**11.30**	0.60	**2.37**	0.76	**2.14**	0.17	0.84
6	Paste	**30.76**	**8.16**	**38.87**	**13.40**	0.76	**1.64**	1.45	**3.52**	0.16	0.96
7	Paste	**19.64**	5.45	**43.00**	**20.75**	0.10	0.96	1.41	**7.19**	0.15	0.90



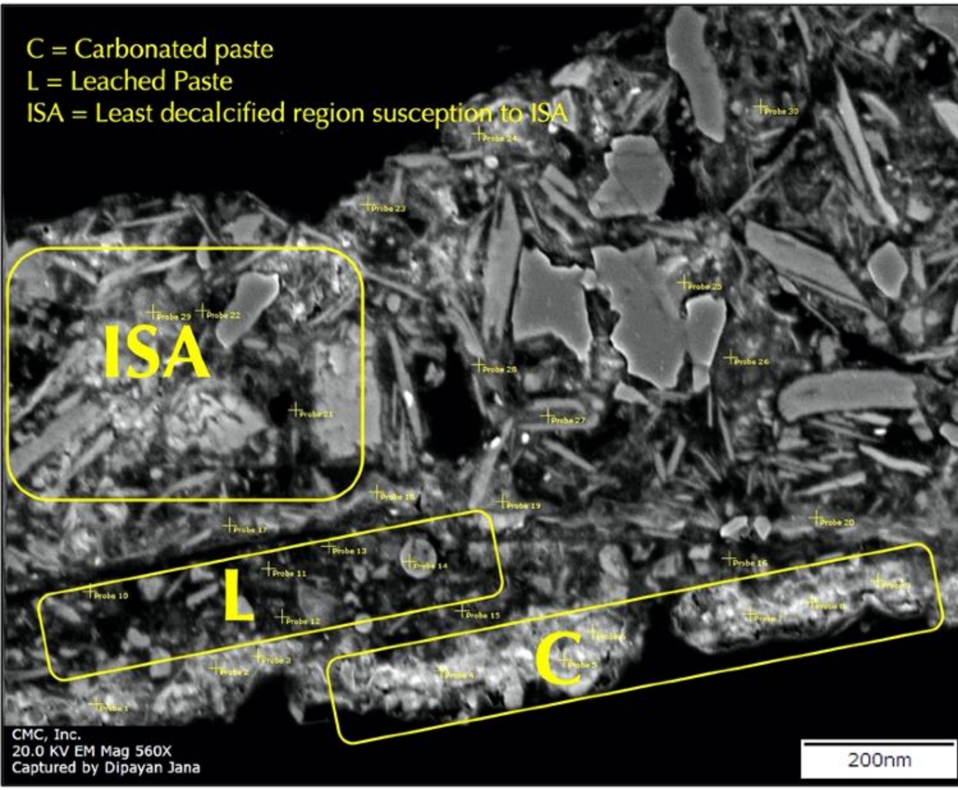
Probe	Phase	O	Ca	Si	Al	Na	Mg	S	K	Ti	Fe
1	Paste	**65.50**	15.65	8.52	0.98	0.00	0.00	8.85	0.03	0.00	0.33
2	Paste	**62.32**	16.29	11.56	0.76	0.00	0.00	8.56	0.00	0.00	0.28
3	Paste	**52.22**	17.04	13.99	5.34	0.00	0.22	9.93	0.20	0.00	0.74
4	Paste	**65.71**	15.96	9.38	0.25	0.00	0.00	8.29	0.02	0.00	0.10

High calcium, silica, and sulfur in paste are from carbonation followed by thaumasite alteration


Paste in Distressed Blocks, Ireland
E/T in Paste and Voids in Distressed Blocks, Ireland
E in Distressed Foundation, CT
Paste in Sound Foundation,Ireland
Paste in Distressed Foundation, CT
ISA = ETG Triangle
Gypsum
Ettringite
Thaumasite
CSH
Portlandite, Calcite
ISA
ISA Products:
Intimately mixed ettringite
and thaumasite
in least decalcified paste
Carbonated
Leached
Leached, decalcified paste rich in Si-Al-Mg (from chlorite) gelatinous residue, free of ettringite/thaumasite
Sound Foundation
Leached Distressed Blocks
S/Ca
Al/Ca
Gypsum CaSO4·2H2O
3CaO·Al2O3·3CaSO4·32H2O
Ettringite
E-ISA vs. T-ISA vs. G-ISA
Monosulfate
Thaumasite CaO.SiO2·CaCO3·CaSO4·15H2O
Monocarbonate
CSH
Portlandite, Calcite

Distressed Block

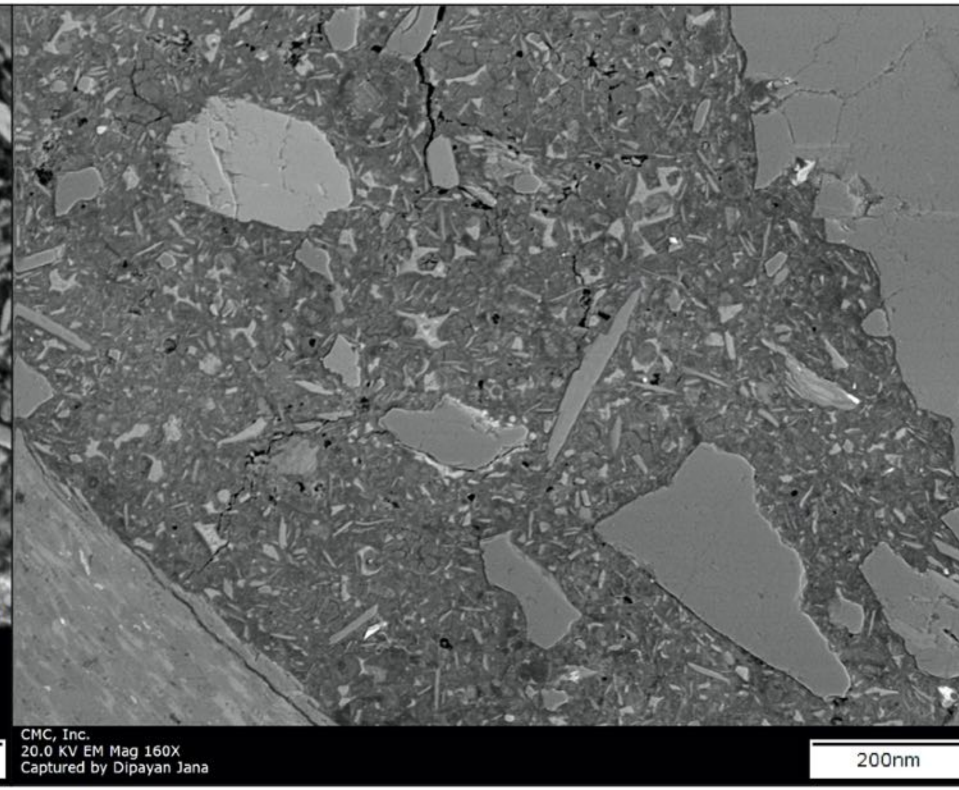
Skeletal Microstructure from Carbonation - Leaching - ISA



Abundant Abraded Phyllite in Mortar
Soft, Porous Paste, Low Paste Volume

Sound Cast-in-place Foundation

Dense Microstructure Free from Carbonation - Leaching - ISA



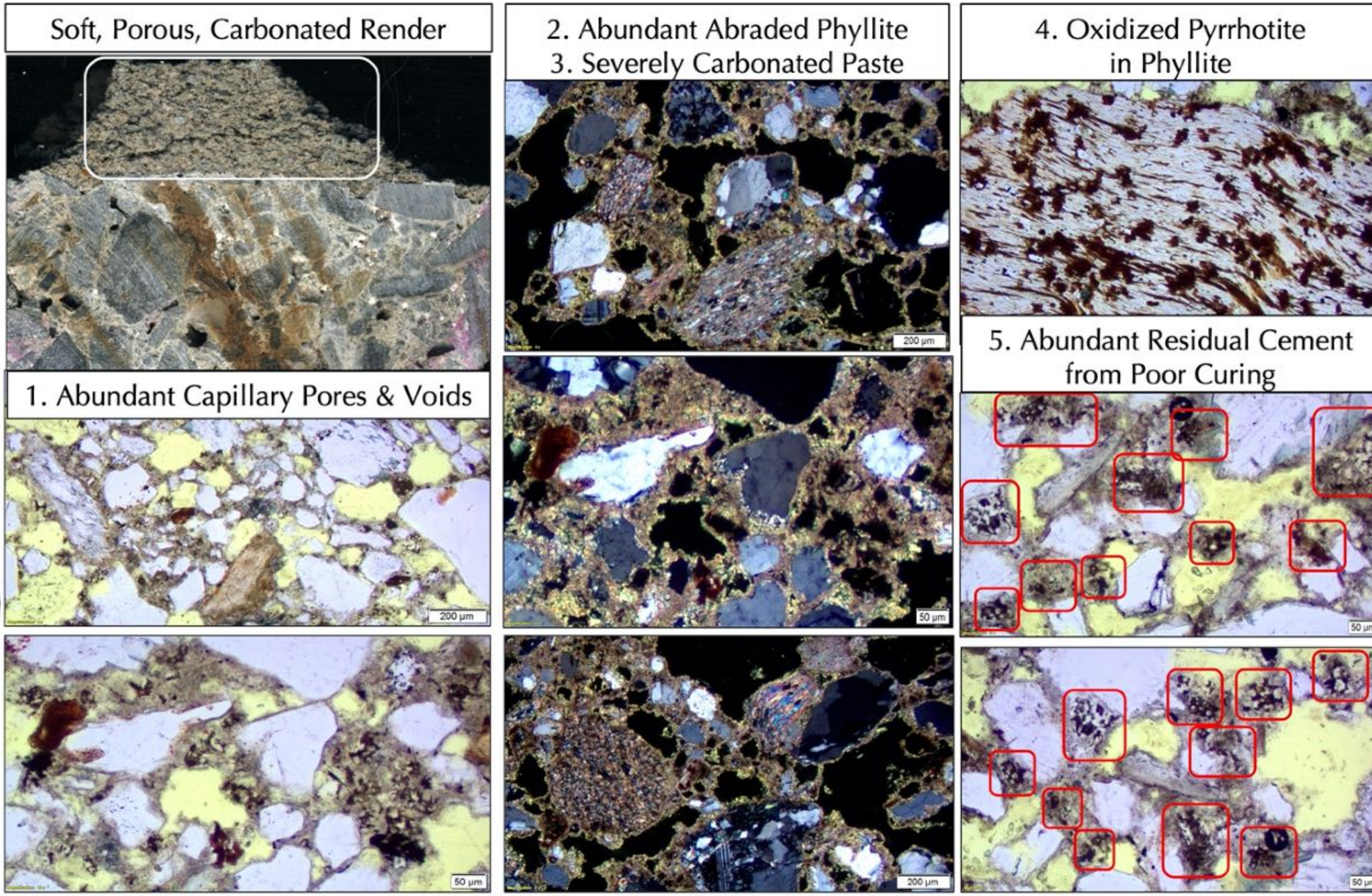
Less Abraded Phyllite in Mortar
Dense Paste, High Paste Volume

5th Culprit - Poor Quality of Sand-Cement Render - The Soft, Cracked Skin!

1. Abundant Capillary Pores (high *w/c*) & Air Voids
2. Abundant Abraded Phyllite
3. Severely Carbonated Paste
4. Oxidized Pyrrhotite in Phyllite
5. Abundant Residual Cement from Poor Curing

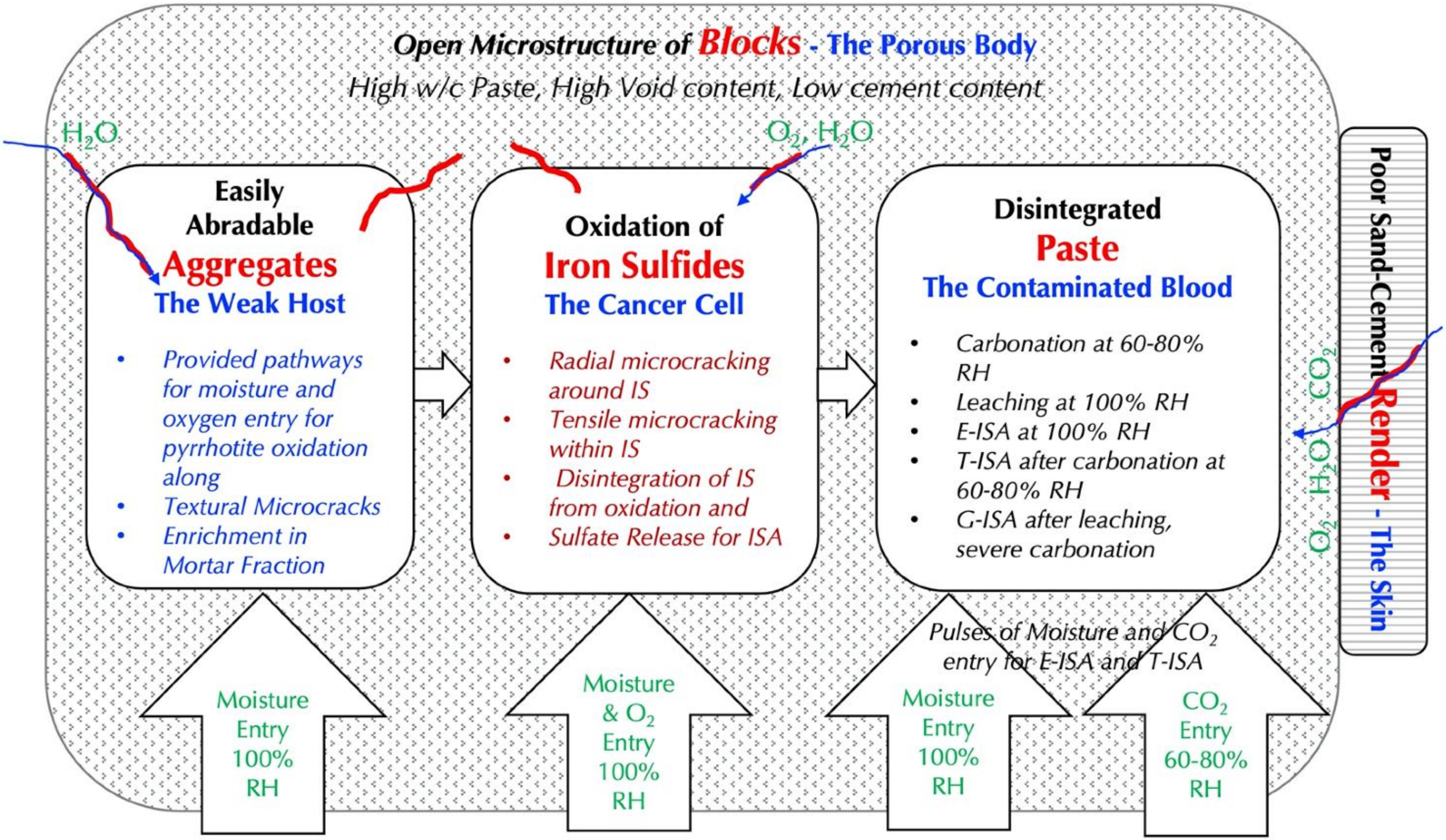
↓

Weak Render



Optical micrographs of deteriorated sand-cement render

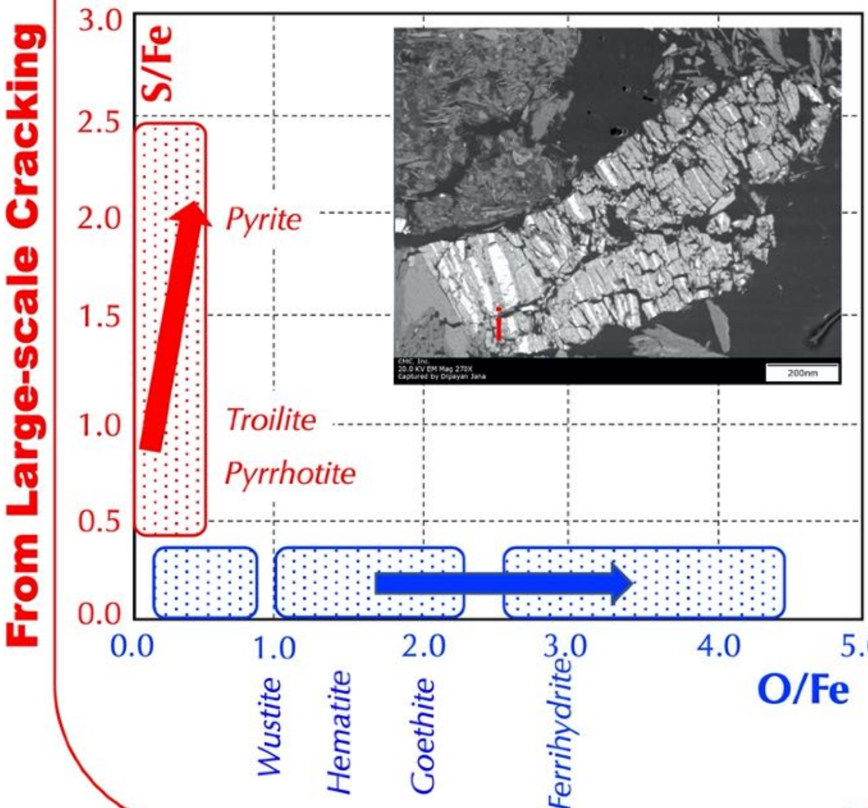
All Five Players in the Holistic Approach



Pyrrhotite Oxidation *versus* Paste Disintegration

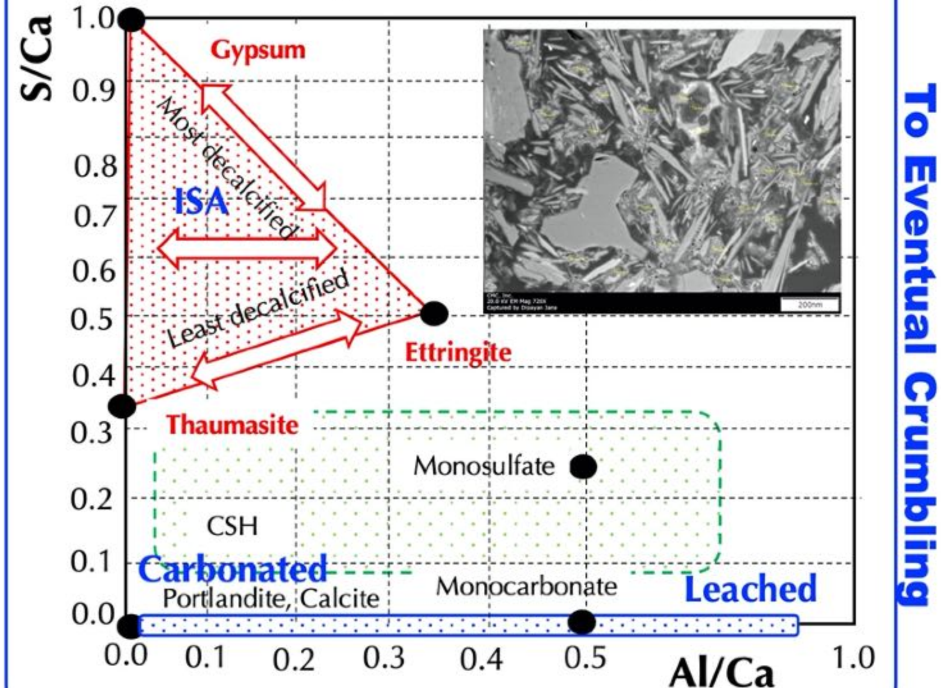
Lion's share - Aggregates 80% by volume

Pyrrhotite Oxidation
(**S/Fe** vs. **O/Fe**)



10% by volume

Paste Deterioration from ISA & Leaching/Decalcification
(**S/Ca** vs. **Al/Ca**)



E-ISA vs. T-ISA vs. G-ISA vs. Leaching

ΔV^{solid} from pyrrhotite oxidation e.g., $Fe(OH)_3$ 6.04 cm^3/mole of sulfide < ΔV^{solid} from ISA, e.g., ettringite 172.19 cm^3/mole of sulfide

www.cmc-concrete.com

www.petrography.net

CMC

Relative Contributions to Distress

Chemical variation trends in S/Fe-O/Fe plot in pyrrhotite and in S/Ca-Al/Ca plot in paste

Applied Petrographic Services, Inc. www.petrography.net

Pyrrhotite Oxidation *versus* Paste Disintegration

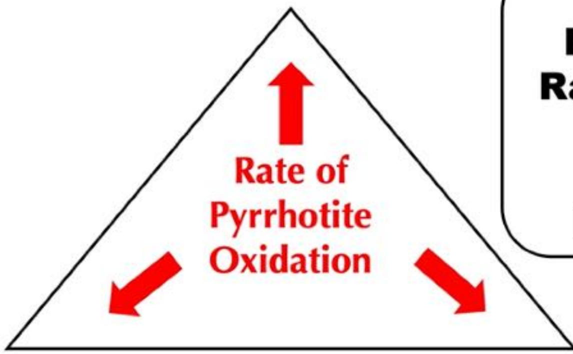
Factors Responsible for Rate of Pyrrhotite Oxidation & Paste Disintegration

From Large-scale Cracking

80% by volume - Lion's share

Aggregate

- Texture (Schistose/Foliated vs Non-Schistose)
- Non-Sulfide Mineralogy
- Sulfide Mineralogy



Pyrrhotite

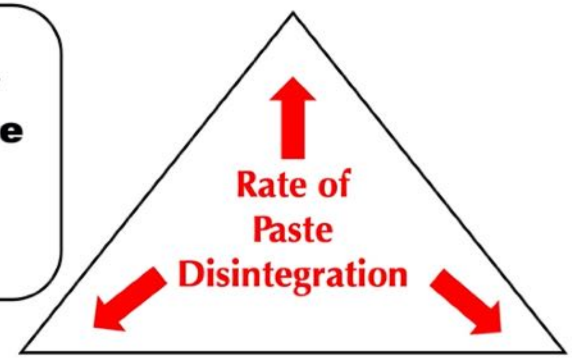
- Crystal Superstructure:
- 4C (Fe_7S_8, Monoclinic) > 5C (Fe_9S_{10}, Hexagonal)
- % Vacancy (12.5% in 4C vs 10% in 5C)
- % Fe^{3+} (28.6% in 4C vs 22.2% in 5C)
- Other Sulfides
- Grain size
- pH, T, Acidophilic Bacteria

Environment

- Open Microstructure of Block
- Concrete permeability
- RH, O_2

10% by volume

Paste Content, *w/cm*, SCM



Environment

- Open Microstructure of Block
- Concrete permeability
- RH, O_2, CO_2

ISA

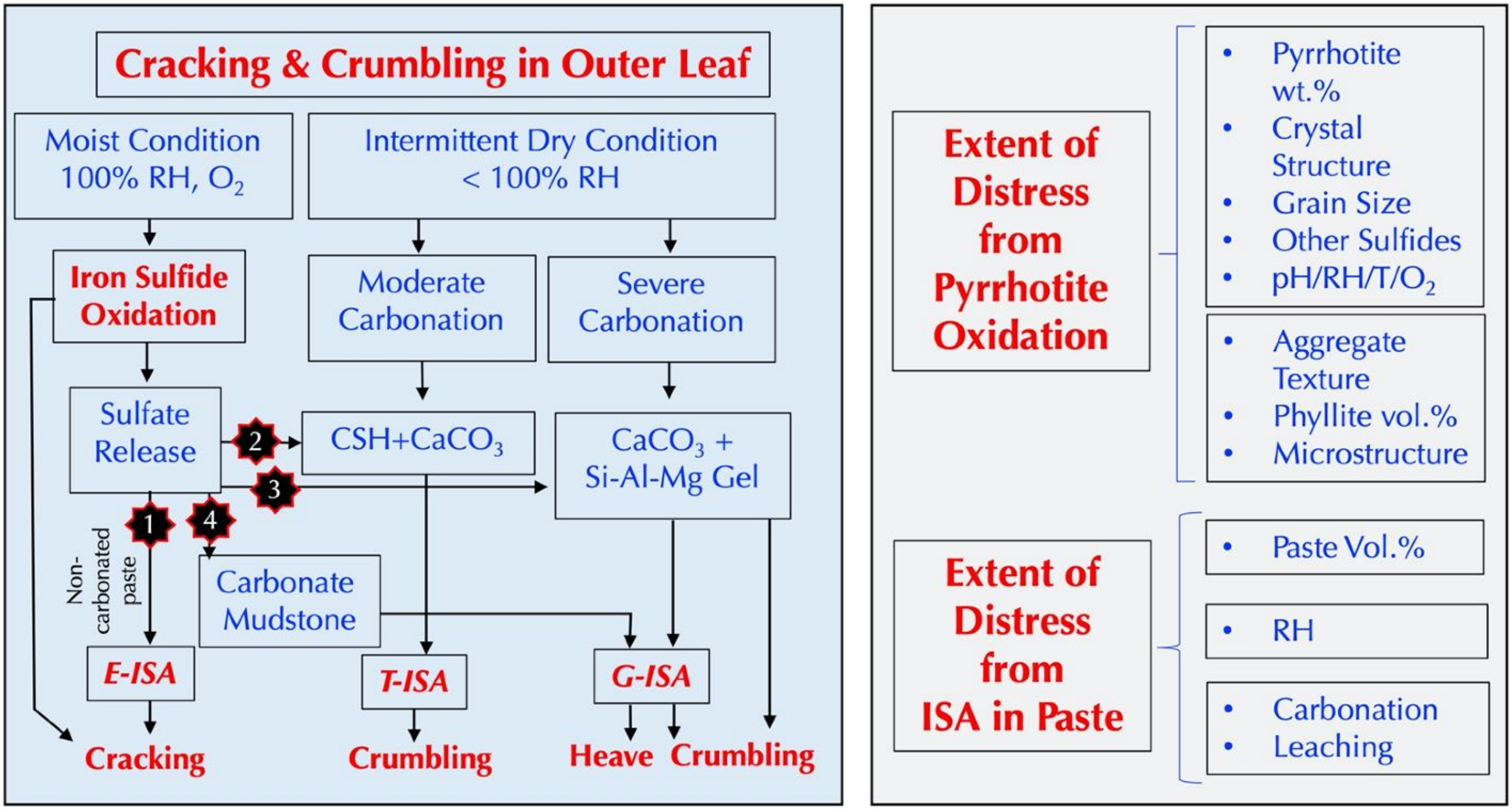
- Pyrrhotite Oxidation
- RH, O_2, CO_2
- E-ISA, T-ISA, G-ISA
- Leaching

To Eventual Crumbling

Reaction Kinetics

When iron goes to rust, sulfide goes to dust…

Putting It Altogether.....



Final Comments

- **Pyrrhotite was undoubted the 'cancer cell' whose deleterious effect was initiated with its presence in the weak phyllite host within the porous microstructure of block for its advanced *oxidation* and sulfate contamination of paste to trigger *ISA,* where render failed to protect the blocks from moisture/O_2/CO_2 entry.**
- **Due to the *larger volume of pyrrhotite-bearing phyllite* compared to the *low-volume of paste*, *distress from pyrrhotite oxidation played the dominant role* in large-scale cracking, which was subsequently aggravated by crumbling of paste from *ISA*.**
- **It is time to take a holistic approach in Ireland instead of 'polarized' views of *wrongfully advertised mica-only* to *rightfully but narrowed down to ISA-only* theories from limited data.**
- **Geologists and petrographers have more important roles to play than engineers since this is, essentially, a petrographic/aggregate issue, which can only be prevented from detailed petrographic examinations of aggregates from quarries and distressed structures. Above all, we need to do good, holistic research, and faithfully transfer scientific evidence into practice.**

Thank you!