

Petrographic Examinations and Chloride Analyses Of Concrete Cores For PRASA (Puerto Rico Aqueduct and Sewer Authority)



Puerto Rico Aqueduct and Sewer Authority (PRASA)
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EXECUTIVE SUMMARY

Reported herein are the results of detailed petrographic examinations and through-depth water-soluble chloride and sulfate contents analyses of five (5) concrete cores. The cores were reportedly collected from five (5) different structural elements of a wastewater treatment plant (WWTP) built in the early 80s, and located in close proximity to the ocean for Puerto Rico Aqueduct and Sewer Authority in Guayama, Puerto Rico. The purposes of the present investigation are to determine the conditions, compositions, and qualities of the concretes in the cores, diagnose evidence of any chemical and/or physical deterioration of concretes in the marine environment, and if so, determine the depths or extents of such deteriorations. The cores were analyzed by detailed petrographic examinations *a la* ASTM C 856, and chemical analysis (anion chromatography *a la* ASTM D 4327) to determine chloride and sulfate contents at various depths for assessment of migration of potentially deleterious agents from the marine environment.

A beneficial protective coating system is detected in four out of five cores received, which have provided the necessary protection of interior concretes from the marine and tank environments. For Core C-C10, as many as three protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, a main intermediate paint coat of nominal 0.5 mm thickness, and, an innermost cementitious coat of 0.2 mm thickness all well-bonded to each other and to the underlying carbonated concrete. For Core P-C4, one uniform paint coat is diagnosed having a nominal thickness of 0.2 mm, which is well-bonded to the underlying carbonated concrete. Immediately beneath the paint, the near-surface region of concrete showed some surface-parallel shrinkage microcracks. For Core PS-C4, three protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, a main intermediate paint coat of nominal 0.5 mm thickness, and an inner cementitious coat of 0.3 mm thickness all well-bonded to each other and to the underlying carbonated concrete. Immediately beneath the paint, as well as within the polymer paint and cementitious layers of coats, and the near-surface region of concrete showed some surface-parallel shrinkage microcracks. For Core T1-C4, as many as four protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, two main intermediate paint coats each of variable but nominal 0.2 mm in thickness where the bottom coat contains calcite fillers in a different resin, followed by the innermost thinner (0.15 mm) coat all well-bonded to each other and to the underlying carbonated concrete. FTIR analysis of the paint coats at the exterior surfaces are determined to be of polyvinyl acetate compositions.

The concrete in all five cores from five different structural elements of the WWTP are found to be compositionally similar and indicative of use of the same concrete mix. The concrete contains: (i) crushed volcanic and volcanoclastic gravel coarse aggregates which are locally available for the volcanic setting of the island, having nominal maximum sizes of $\frac{3}{4}$ in. Particles are well-graded, well-distributed, subangular to subrounded, sound, and show many typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite-rhyolite clan typically found in a volcanic island setting on an active subduction zone, (ii) natural siliceous sand fine aggregate with some calcareous seashells and finer fractions of volcanic rock fragments, (iii) Portland cement pastes, having cement contents estimated to be $5\frac{1}{2}$ to 6 bags per cubic yard, without any other pozzolanic or cementitious materials, and water-cement ratios



uniform throughout the depth of each core and estimated to be 0.40 to 0.45, and (iv) many interstitial voids except any intentionally introduced entrained air for the concretes to be non-air-entrained (estimated 1 to 3 percent total air).

Despite the reported location of the plant in a marine environment and the nature of its past usage, all five cores showed negligible chloride contents at the exposed ends and in the interiors to remove the possibility of chloride-induced corrosion of reinforcing steel in concrete. Any steel corrosion would then be carbonation-induced, which probably would have occurred prior to the placement of protective coats. The present cores showed up to 15 mm deep carbonation beneath the protective coats, which if gets deeper in some locations to depths of reinforcing steel can reduce the inherent alkalinities of paste to destroy the protective iron oxide films around the steel to cause initiation of corrosion in the presence of oxygen and moisture. Sulfate contents are indicative of sulfates from Portland cement with no introduction of an excess sulfate from the marine environment or wastewater containments in the plant.

The overall condition of the interior concretes in all five cores are found to be sound and serviceable mainly due to the beneficial performance of protective coatings to prevent any migration of elements from the environments. Based on deep carbonation in cores to depths of 15 mm as well as some near-surface microcracking at the top 15 mm of exposed surfaces, carbonation-induced corrosion of steel may have occurred to cause cracking and spalling from rebar corrosion, but none of the cores showed any elevated chloride to cause any chloride-induced corrosion. The overall qualities and conditions of concretes in the main bodies of cores are judged to be sound with no evidence of any physical or chemical deterioration. The interior concretes are dense, well-consolidated, and should be serviceable in their intended environment as long as they are well-protected by the protective coatings to prevent penetration of moisture, chloride, and other corrosive agents to cause further corrosion of steel, and corrosion-related cracking and spalling.

INTRODUCTION

Reported herein are the results of detailed petrographic examinations and through-depth water-soluble chloride and sulfate contents analyses of five (5) concrete cores collected from five (5) different structural elements of a wastewater treatment plant (WWTP) built in the early 80s and located in close proximity to the ocean for Puerto Rico Aqueduct and Sewer Authority in Guayama, Puerto Rico.

BACKGROUND INFORMATION

The subject wastewater treatment plant (WWTP) was reportedly built in early 80's. The channel structure has spalling due to rebar corrosion and concrete deterioration. A total of five cores were extracted, one per each structure. A total of six (6) structures/rooms are located near to the beach. The purpose of this investigation is to assess the status of the concrete in the structural elements to evaluate the concrete durability including the potential carbonation and/or chloride-induced corrosion of reinforcing steel in concrete. As part of complete remodeling of the WWTP the present investigation is done to determine which of the structures under investigation require repair, which are beyond repair, and which are sound. Spalling of concrete is reported in the channel beams. No spalling is observed at the walls where the cores were taken, but need to investigate the status of the concrete. WWTP is directly exposed to chemicals and corrosive environment due to wastewater processes and its proximity to the ocean.



Figure 1: Field photos of five structural elements of wastewater treatment plant from where five concrete cores for this study were reportedly retrieved. The core ID received for each structure is marked.

PURPOSES OF PRESENT INVESTIGATION

The purposes of the present investigation are to determine the conditions, compositions, and qualities of the concretes in the cores, diagnose evidence of any chemical and/or physical deterioration of concretes in the cores, and if so, determine the depths or extents of such deteriorations.

METHODOLOGIES

PETROGRAPHIC EXAMINATIONS

The concrete cores were examined by detailed petrographic (microscopical) examinations by following the methods of ASTM C 856 “Standard Practice for Petrographic Examination of Hardened Concrete.”

Details of concrete petrography, and sample preparation techniques for petrographic examinations of concrete are provided in Jana (2006).

Briefly, the steps followed during petrographic examination of the samples include:

- i. Visual examinations of samples, as received;
- ii. Low-power stereo-microscopical examinations of as-received, saw-cut, and freshly fractured sections, and lapped cross sections of samples for evaluation of textures, and compositions, and diagnosis of any distress;
- iii. Examinations of oil immersion mounts in a petrographic microscope for mineralogical compositions of specific areas of interest;
- iv. Examinations of blue dye-mixed (to highlight open spaces, cracks, voids, etc.) epoxy-impregnated large area (50 mm × 75 mm) thin sections of concretes in a petrographic microscope for detailed compositional and microstructural analyses;
- v. Determination of depth of carbonation and other alterations of paste from the surfaces in contact with the oceanfront elements;
- vi. Photographing the samples, as received and at various stages of preparation with digital camera and scanner;
- vii. Micrographs of lapped sections and thin sections of samples taken with stereomicroscope and petrographic microscope, respectively, to provide detailed compositional and mineralogical information of concrete.
- viii. A Jenoptik Progres GRYPHAX camera attached to a Nikon Eclipse 600 POL petrographic microscope (equipped with reflected, transmitted, polarized and fluorescent-light facilities), a Jenoptik Progres C14 camera attached to an Olympus SZH reflected and transmitted-light stereomicroscope, and an OMAX digital camera attached to a Nikon SMZ-10A low-power stereomicroscope were used together for detailed optical microscopical examinations and associated digital photomicrography (Figure 2).



Figure 2: CMC's optical microscopy lab that houses microscopes used in this study.

WATER-SOLUBLE CHLORIDE AND SULFATE CONTENTS

The exposed ends, the mid-depth locations, and the bottom ends of cores were selected for determination of water-soluble chloride and sulfate contents of concrete. The purposes of such sample selection are: (a) to determine the effectiveness of protective coatings in mitigation of migration of chloride, moisture and other corrosive agents into the concrete since its installation, and, (b) determination of chloride levels present inside the concrete for evaluating the potential for future chloride-induced corrosion of reinforcing steel in concrete.

Samples were selected by trimming small pieces from each depth with a water-cooled diamond saw. Trimmed pieces were pulverized down to finer than 0.3 mm size. Approximately 10 grams of pulverized sample was thoroughly digested in 100 ml deionized water first in near-boiling temperature for 15 minutes with magnetic stirrer, followed by further room-temperature digestion for a period of 24 hours.

The digested sample solution was then filtered under vacuum, first through two 2.5-micron filter papers, followed by another filtration through two 0.2-micron filter papers to collect the filtrate. The filtrate thus obtained was diluted to a final volume of 200 ml in a volumetric flask. The filtrates thus prepared were used for potentiometric titration with a silver nitrate titrant *a la* ASTM C 1218 by using Metrohm 916 Ti-Touch

titration or 848 Titrando apparatus with attached 814 auto sample processor to determine the chloride contents, and/or by ion chromatography by following the methods of ASTM C 4327 using Metrohm 881 Compact IC Professional with 858 professional sample processor (Figure 3). The instruments were calibrated with standard chloride and sulfate solutions of known concentrations.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

The compositions of protective paint coats on some cores were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) with a Perkin Elmer Spectrum 100 FTIR with the attached Universal Attenuated Reflectance (UATR) module.

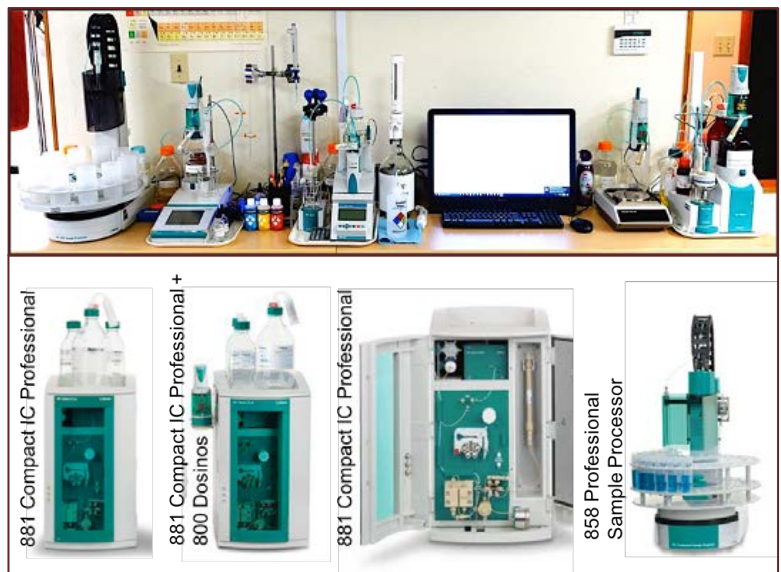


Figure 3: Set-ups for fully automated chloride analysis of concrete by potentiometric titration (top) and chloride and sulfate analysis by ion chromatography (bottom).

**SAMPLES****PHOTOGRAPHS, IDENTIFICATION, INTEGRITY, AND DIMENSIONS**

Core ID	Structure	Core Diameter (in.)	Core Length (in.)	Top Exposed Surface	Bottom Surface	Cracking	Reinforcing Steel	Representing Condition
C-C10	Channel	2 in. (50 mm)	6½ in. (170 mm)	Light Green Paint	Fresh Fractured	Cracked at 80 mm from painted top surface	None	Intact, Ring Resonance, Dry, One crack in the middle
P-C4	PIT	2½ in. (65 mm)	6½ in. (170 mm)	Tan Painted	Fresh Fractured	None	None	Intact, Ring Resonance, Dry, No visible Cracking
PS-C4	Pump Station	2 in. (50 mm)	6½ in. (170 mm)	Tan Painted	Fresh Fractured	None	None	Intact, Ring Resonance, Dry, No visible Cracking
PR-C4	Recirculation Pump Station	2 in. (50 mm)	6 in. (150 mm)	Weathered Gray	Fresh Fractured	None	None	Intact, Ring Resonance, Dry, No visible Cracking
T1-C4	Anaerobic Tank 1	2 in. (50 mm)	5¾ in. (145 mm)	Turquoise Blue paint	Fresh Fractured	None	None	Intact, Ring Resonance, Dry, No visible Cracking

Table 1: Descriptions of five cores, as received. Figures 4 to 8 show conditions of five cores as received.

END SURFACES

Cores C-C10 (from Channel), P-C4 (from PIT), PS-C4 (from Pump Station), PR-C4 (from Recirculation Pump Station), and T1-C4 (Anaerobic Tank) showed some sort of protective coatings on the exposed surfaces to protect the interior concretes from migration of potentially deleterious agents from the environment. These coats are either a single coat, or multiple coats, a light green paint in C-C10, a tan-colored paint in P-C4 and PS-C4, and a turquoise paint in T1-C4, mostly applied over an interior coat. The opposite bottom ends are fresh fractured.

CRACKING & OTHER VISIBLE DISTRESS, IF ANY

Core C-C10 was broken in the middle into two halves which probably occurred during the coring operations. Other four cores were received in intact crack-free conditions.

EMBEDDED ITEMS

None of the five cores received showed the presence of any steel reinforcement, wire mesh, fibers, or any other embedded items.

RESONANCE

The cores have a ringing resonance, when hammered.



Figure 4: Shown are the exterior painted surface (top left), interior fractured end (top right) and side cylindrical surfaces of the Core C-C10 from Channel.

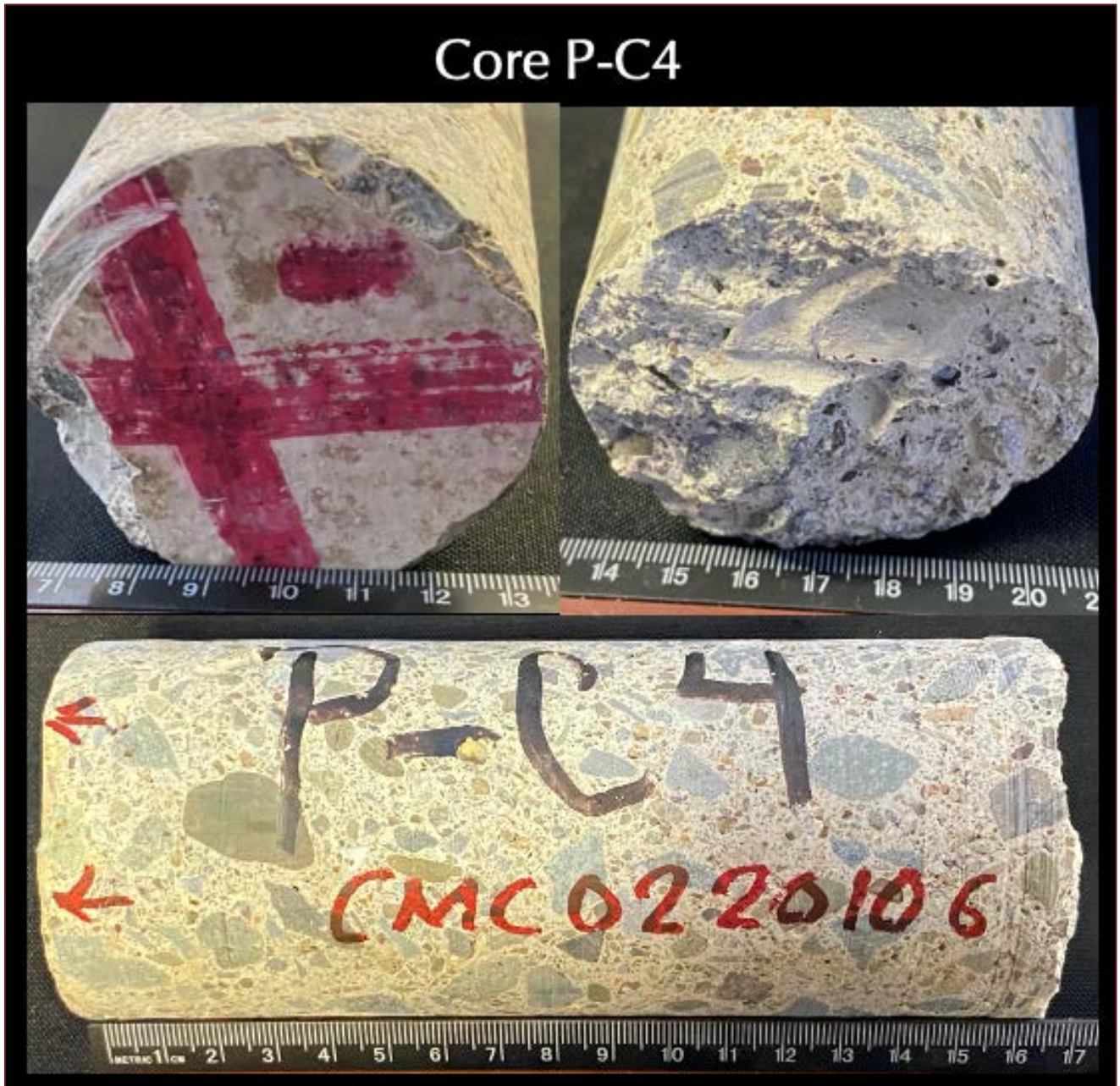


Figure 5: Shown are the exterior painted surface (top left), interior fractured end (top right) and side cylindrical surfaces of the Core P-C4 from PIT.

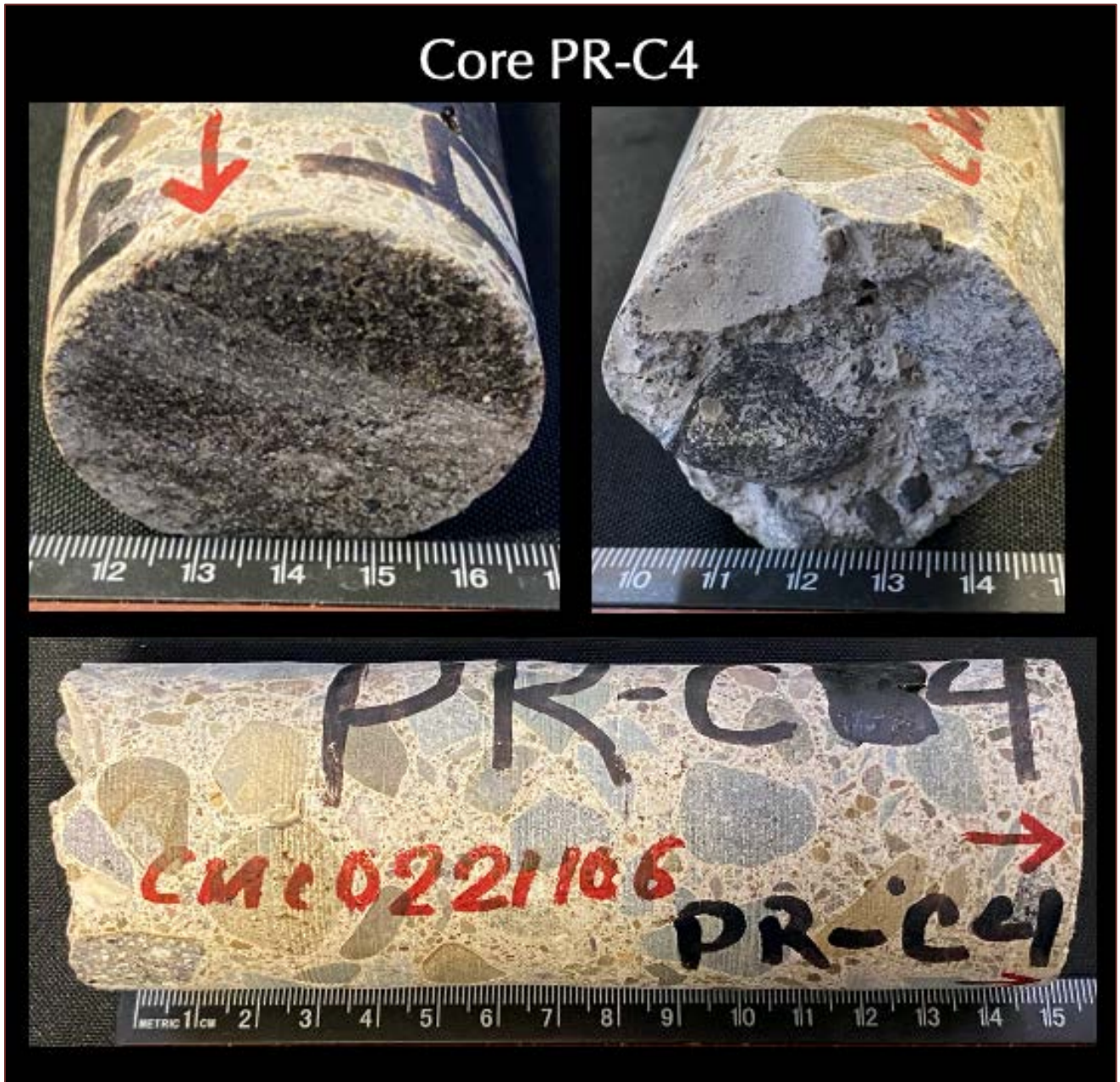


Figure 6: Shown are the exterior weathered grey surface (top left), interior fractured end (top right) and side cylindrical surfaces of the Core PR-C4 from Recirculation Pump Station.

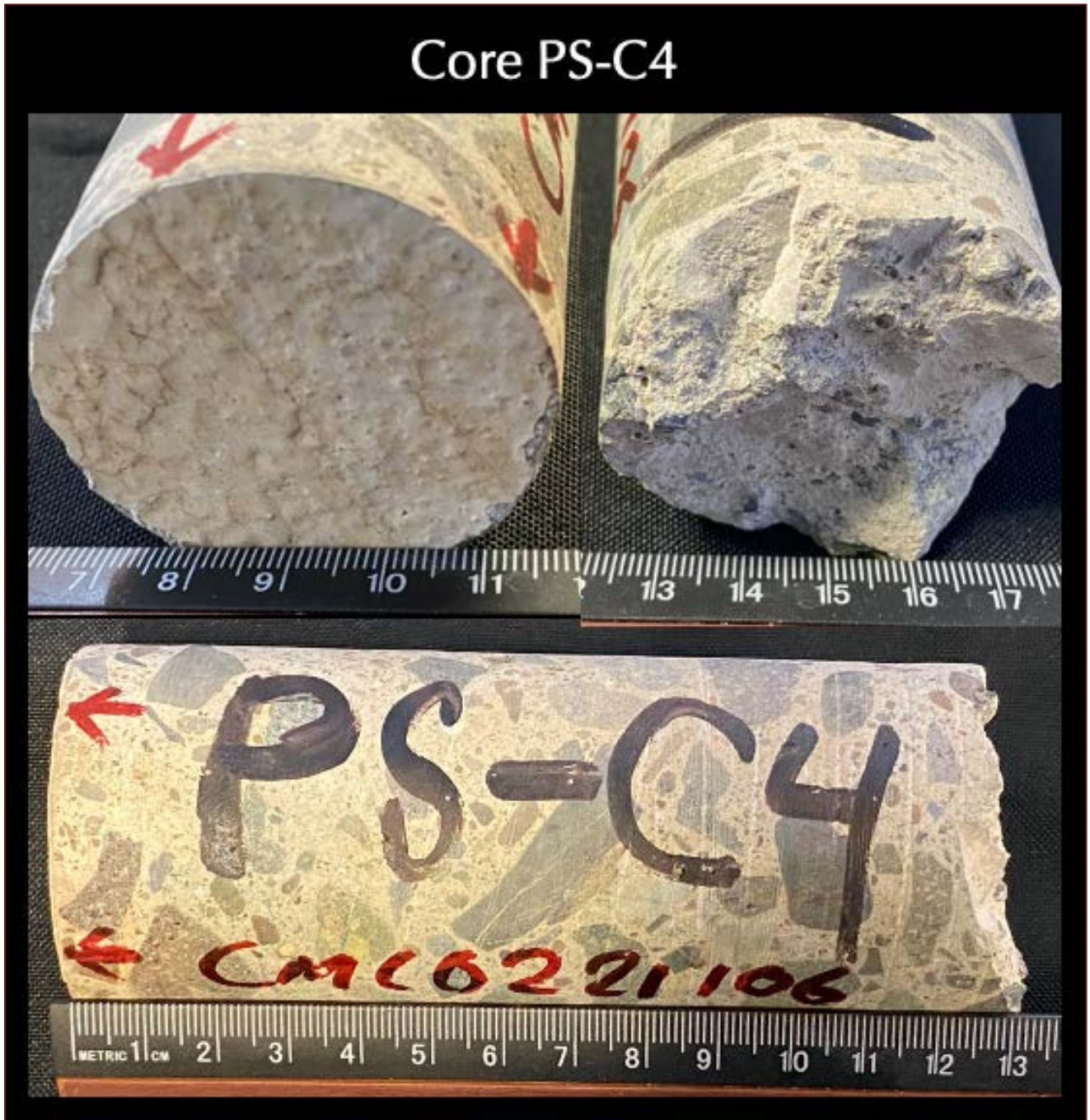


Figure 7: Shown are the exterior painted surface (top left), interior fractured end (top right) and side cylindrical surfaces of the Core PS-C4 from Pump Station.

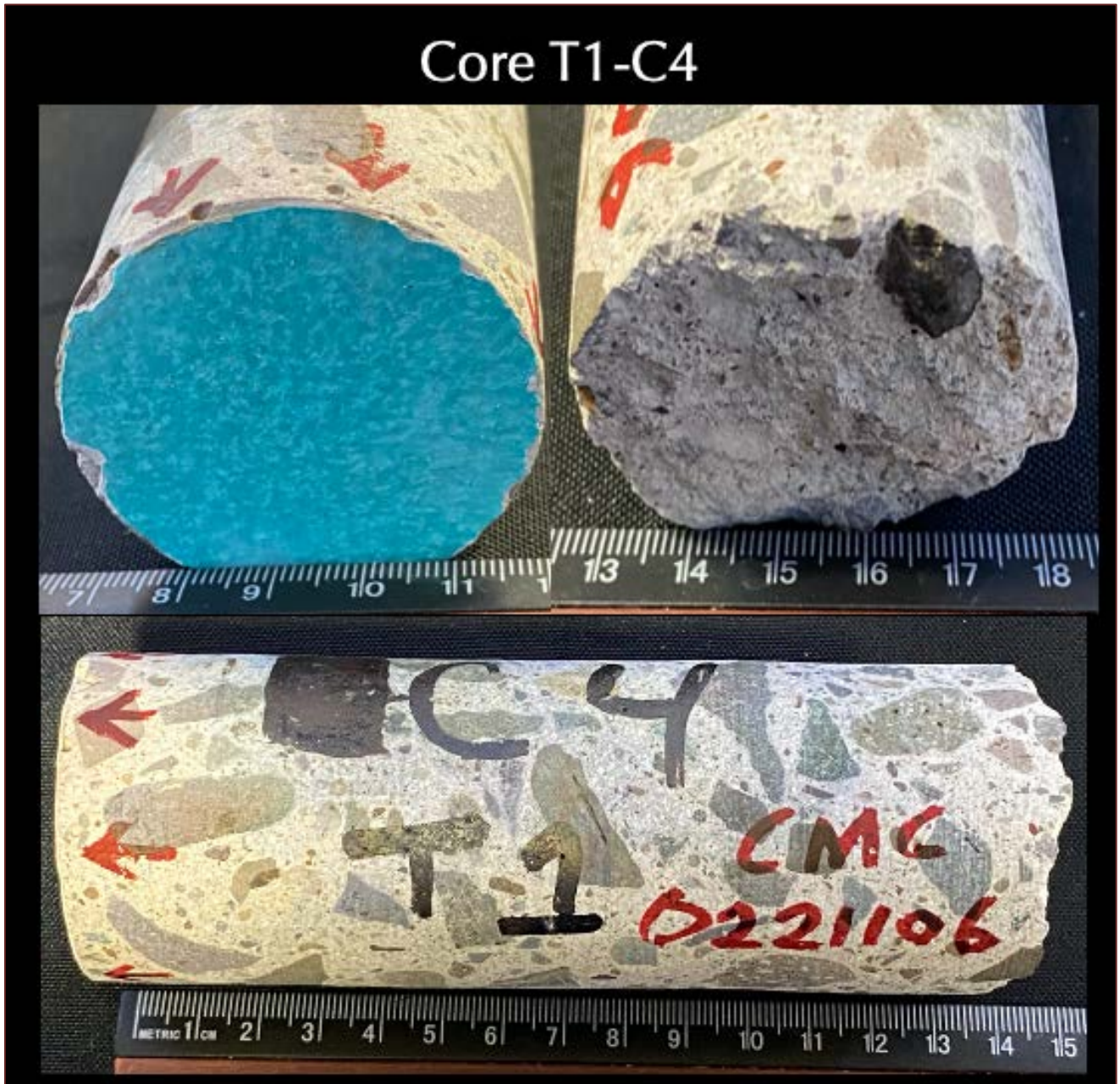


Figure 8: Shown are the exterior painted surface (top left), interior fractured end (top right) and side cylindrical surfaces of the Core T1-C4 from Anaerobic Tank 1.

PETROGRAPHIC EXAMINATIONS

LAPPED CROSS SECTIONS



Figure 9: Lapped cross section of Core C-C10 showing:

- (a) A thin **paint coat** at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm;
- (b) The **main concrete body** containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and,
- (c) The overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body.

The boxed area at left is enlarged at right.

The beige discoloration of paste at the top 15 mm beneath the protective coating is due to atmospheric carbonation of paste prior to the application of protective coating.



Figure 10: A second lapped cross section of Core C-C10 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right. The beige discoloration of paste at the top 10 mm beneath the protective coating is due to atmospheric carbonation of paste prior to the application of protective coating.

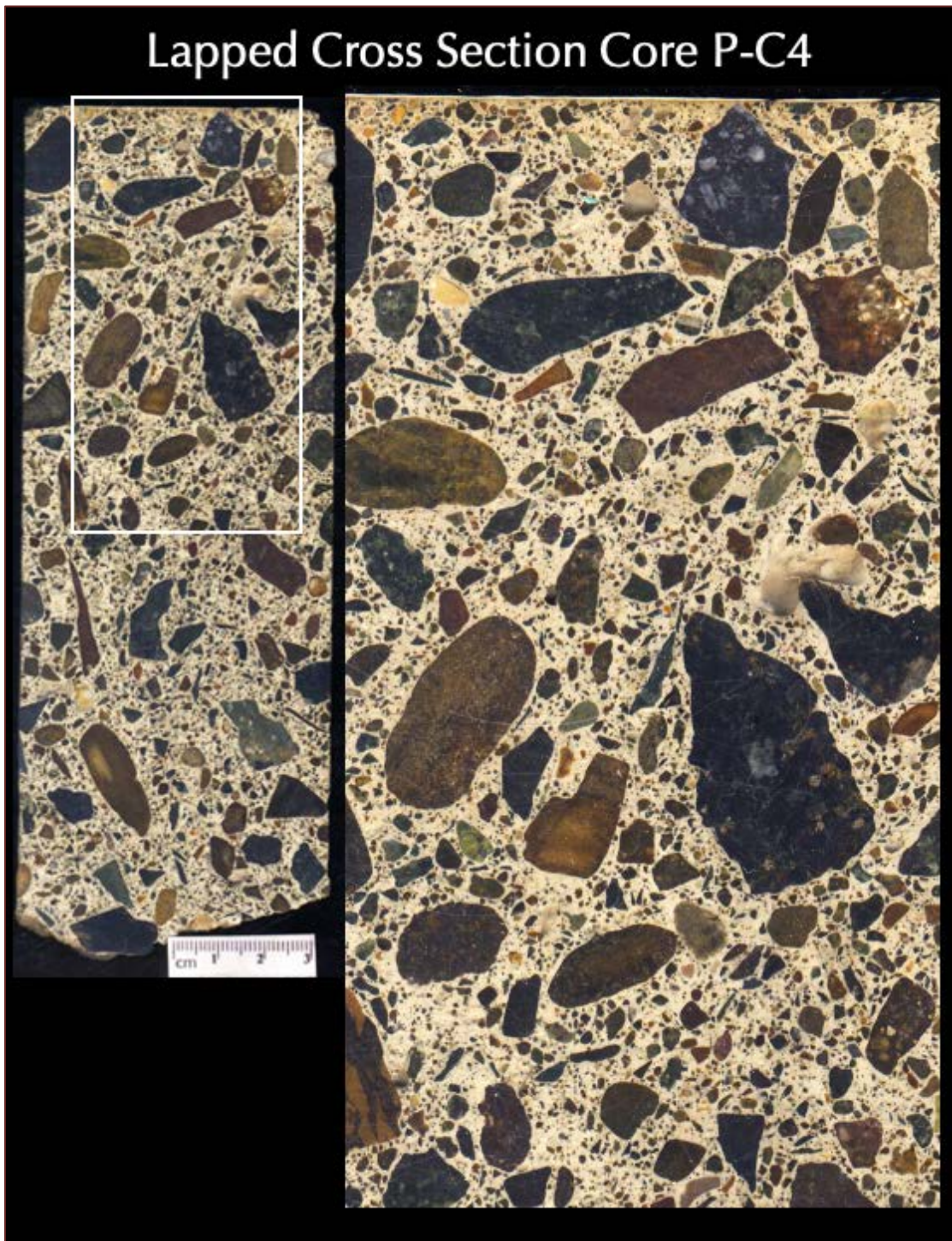


Figure 11: Lapped cross section of Core P-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right. The beige discoloration of paste at the top 15 mm beneath the protective coating is due to atmospheric carbonation of paste prior to the application of protective coating.

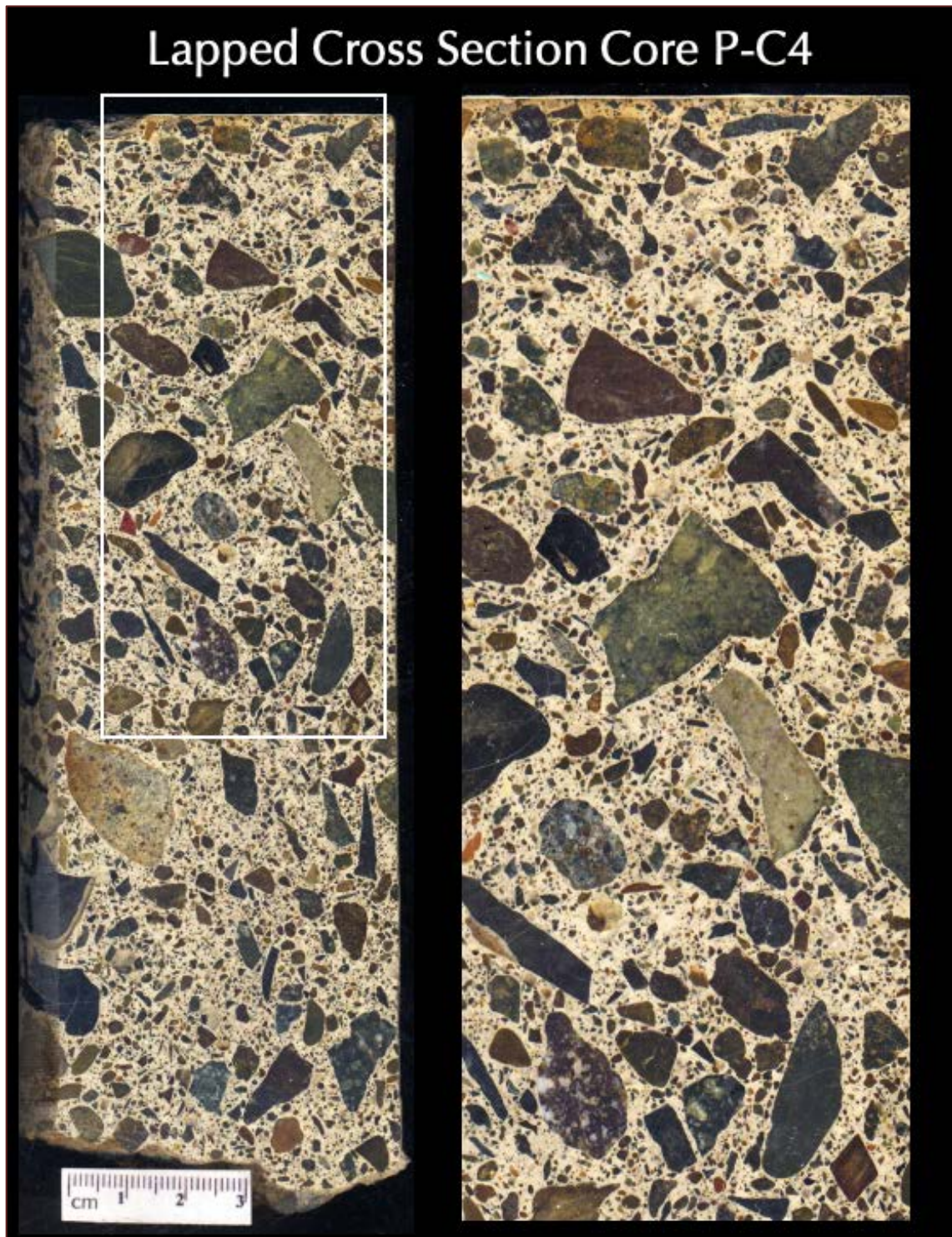


Figure 12: A second lapped cross section of Core P-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right. The beige discoloration of paste at the top 10 mm beneath the protective coating is due to atmospheric carbonation of paste prior to the application of protective coating.



Figure 13: Lapped cross section of Core PR-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.

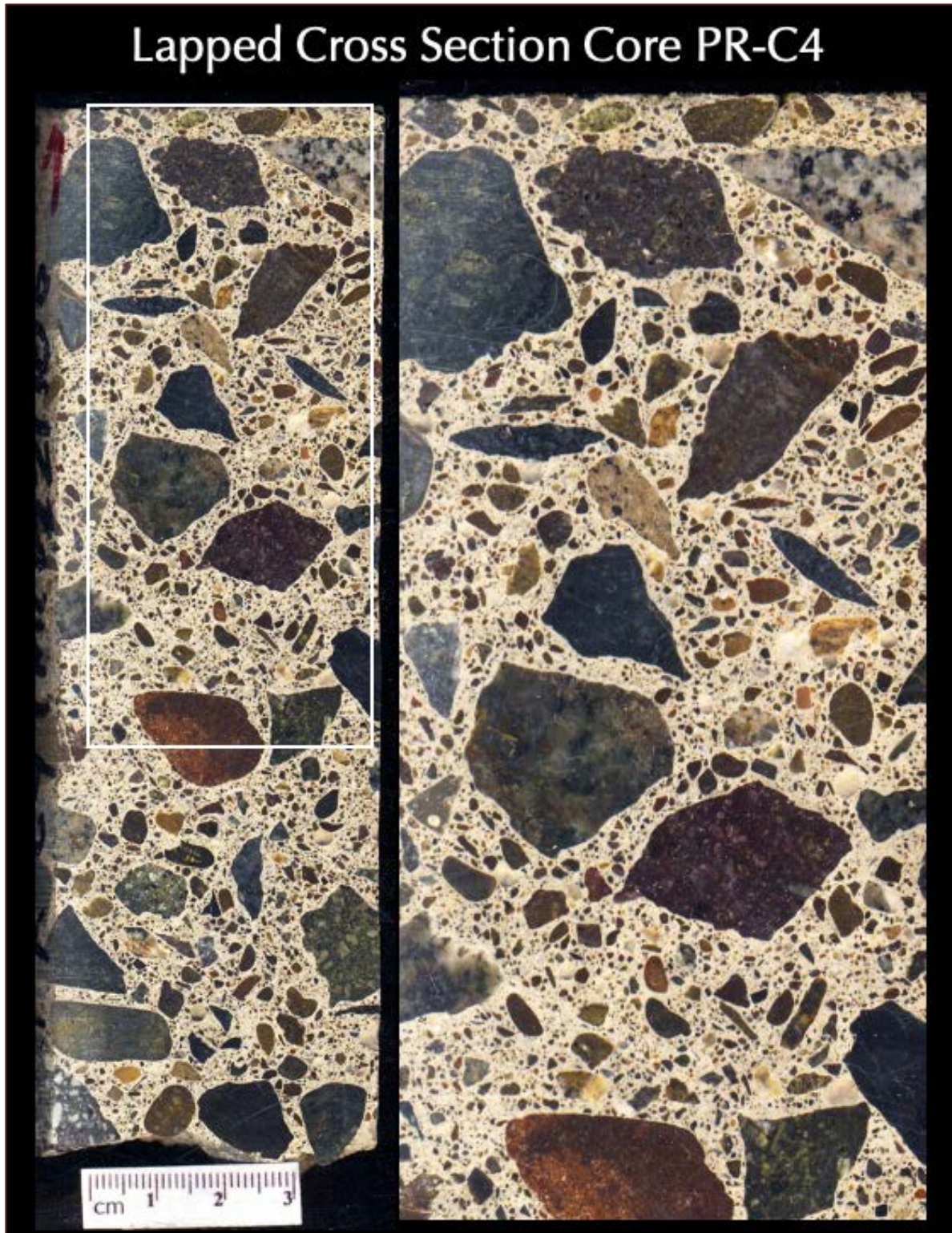


Figure 14: A second lapped cross section of Core PR-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.



Figure 15: Lapped cross section of Core PS-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.



Figure 16: A second lapped cross section of Core PS-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.



Figure 17: Lapped cross section of Core T1-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.

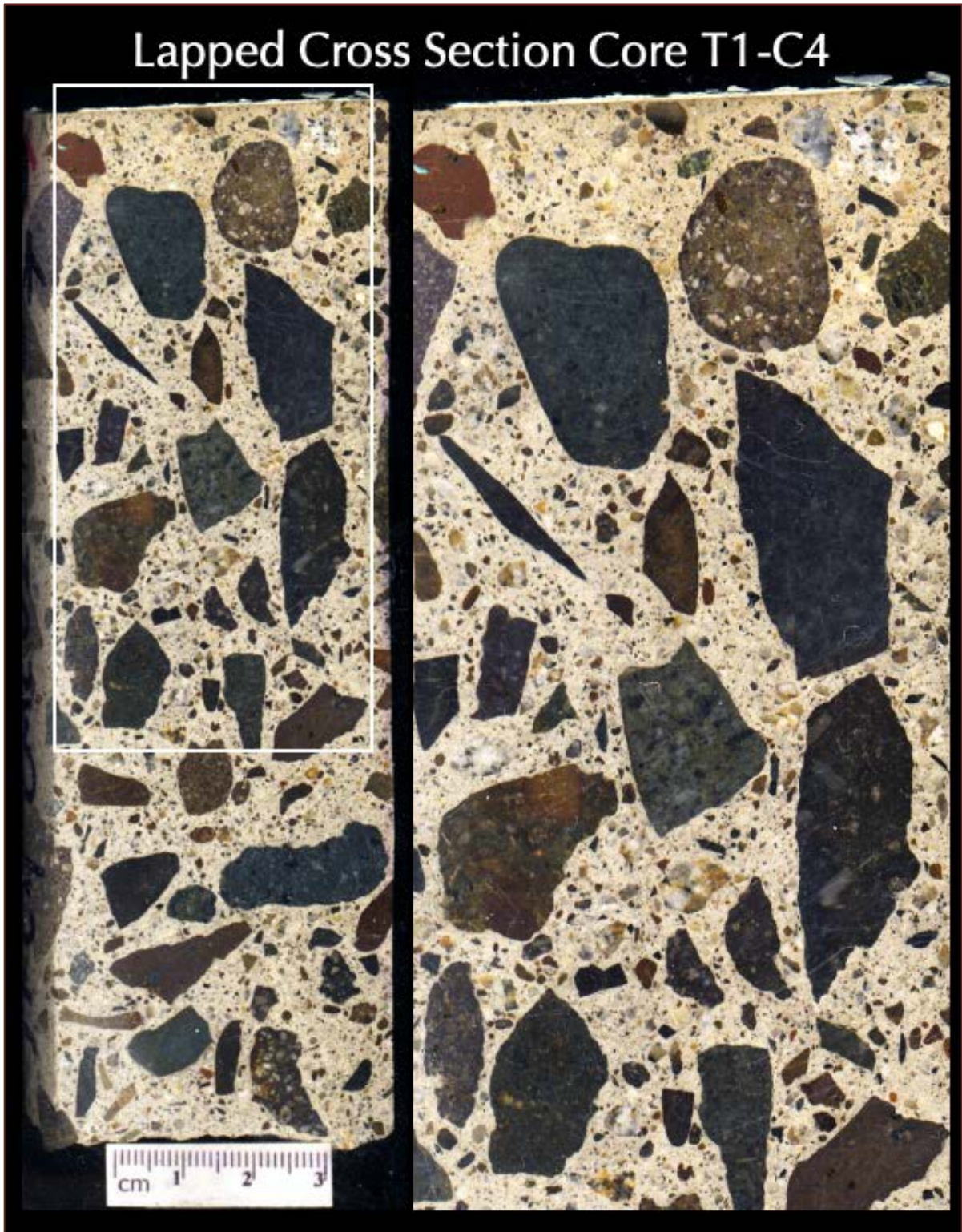


Figure 18: A second lapped cross section of Core T1-C4 showing: (a) a thin paint coat at the top well-bonded to the underlying concrete having a nominal thickness of < 1 mm; (b) the main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste; and, (c) the overall sound (visually crack-free), dense, well-consolidated nature of the concrete in the body. The boxed area at left is enlarged at right.

MICROGRAPHS OF LAPPED CROSS SECTIONS

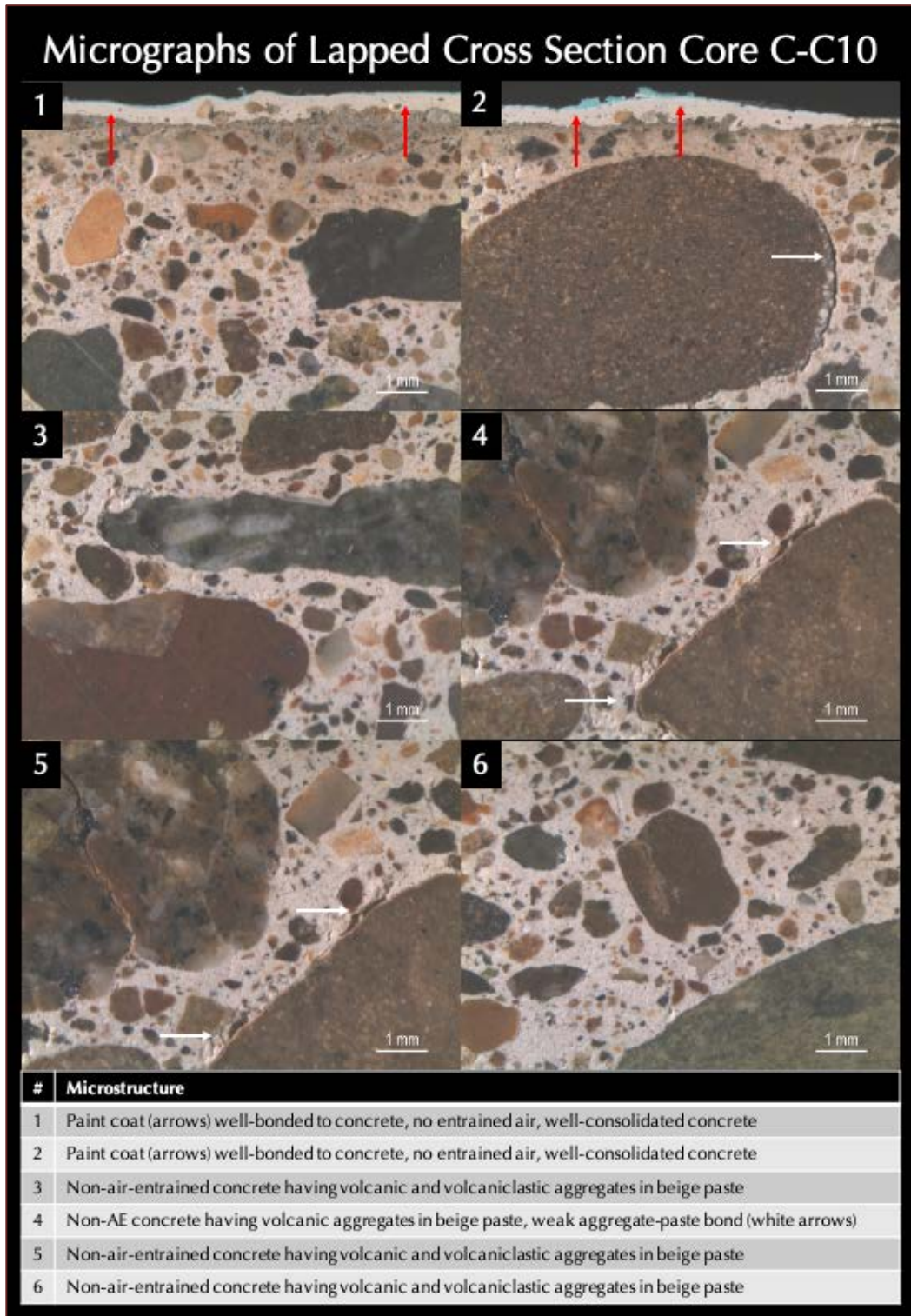


Figure 19: Micrographs of lapped cross section of the Core C-C10 showing:

(a) The paint coat at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm; and,

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint.

Scale bars are 1 mm.

Micrographs of Lapped Cross Section Core C-C10

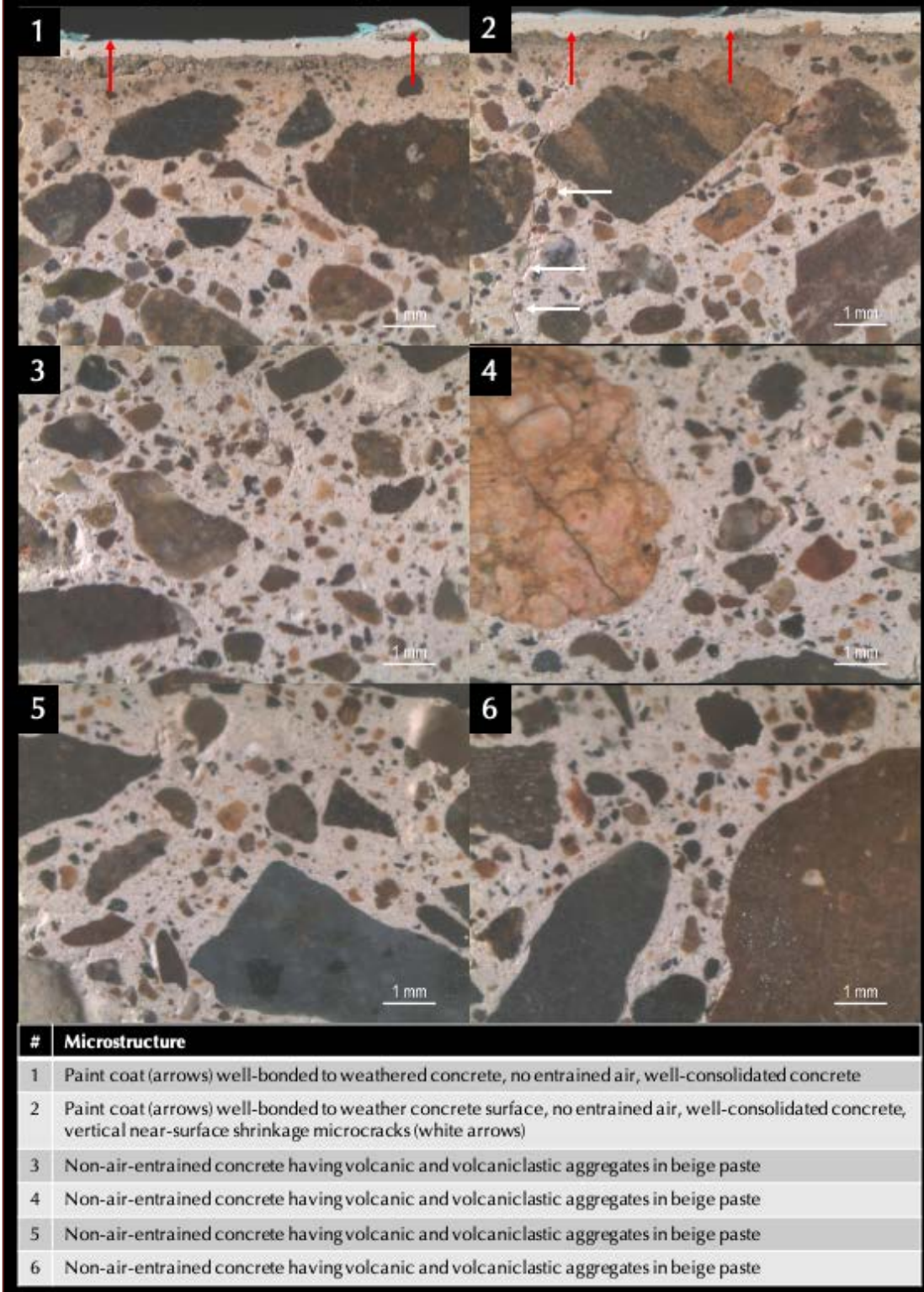


Figure 20: Micrographs of lapped cross section of the Core C-C10 showing:

(a) The paint coat at the top bonded to the main concrete body;

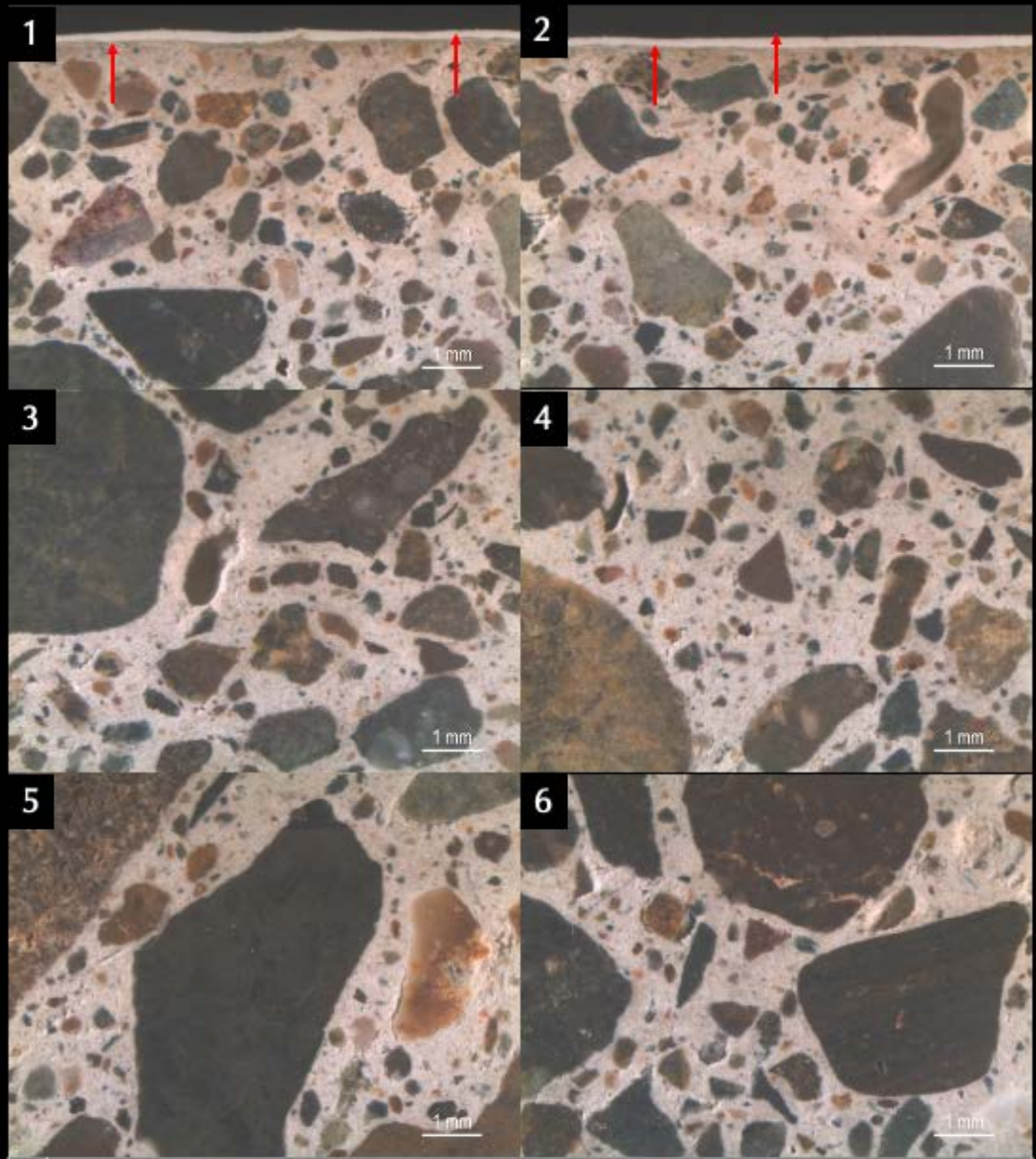
(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm; and,

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint.

Scale bars are 1 mm.

Micrographs of Lapped Cross Section Core P-C4



#	Microstructure
1	Paint coat (arrows) well-bonded to concrete, no entrained air, well-consolidated concrete
2	Paint coat (arrows) well-bonded to concrete, no entrained air, well-consolidated concrete
3	Non-air-entrained concrete having volcanic and volcanoclastic aggregates in beige paste
4	Non-air-entrained concrete having volcanic and volcanoclastic aggregates in beige paste
5	Non-air-entrained concrete having volcanic and volcanoclastic aggregates in beige paste
6	Non-air-entrained concrete having volcanic and volcanoclastic aggregates in beige paste

Figure 21: Micrographs of lapped cross section of the Core P-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm; and,

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint.

Scale bars are 1 mm.

Micrographs of Lapped Cross Section Core P-C4

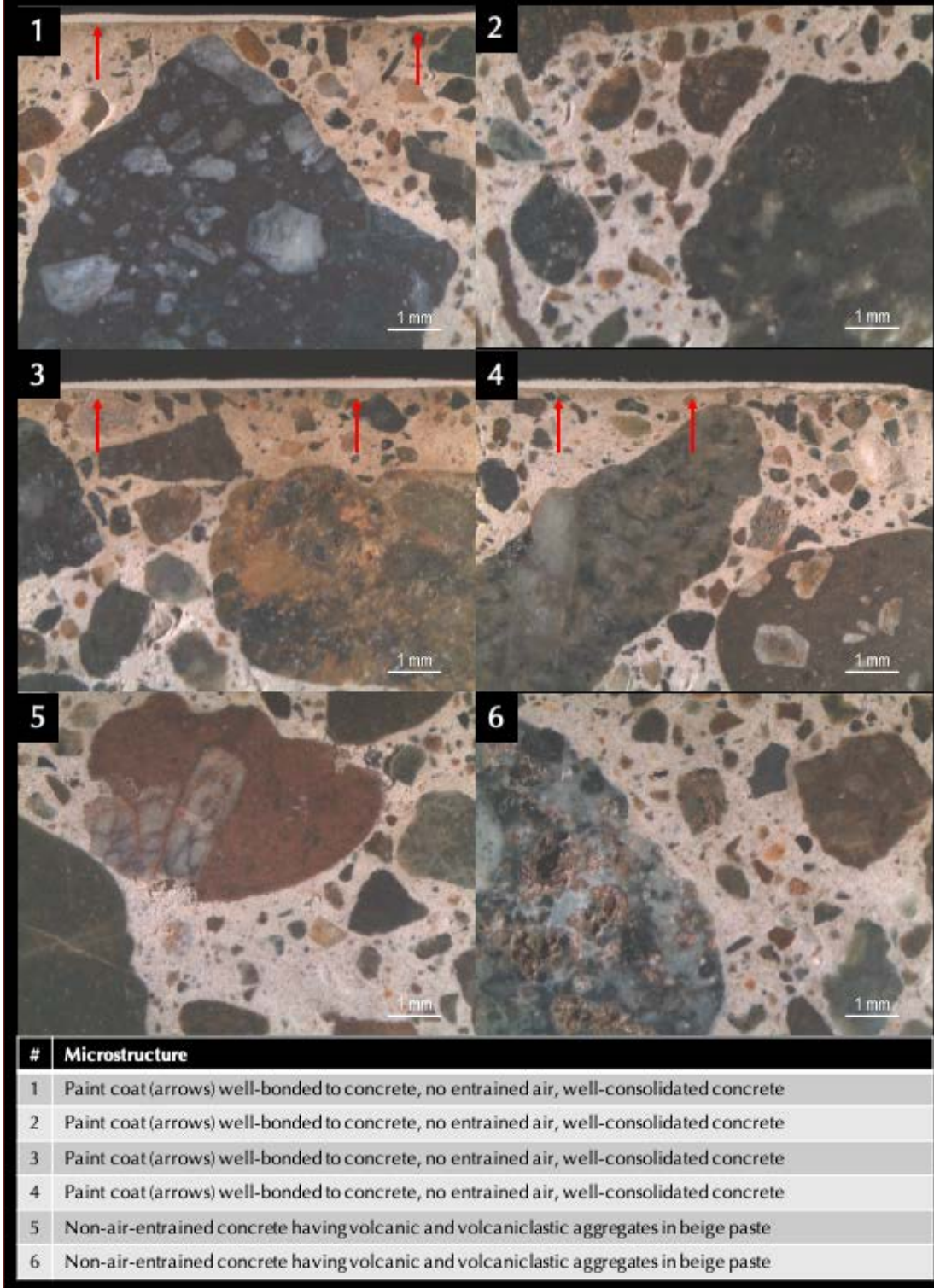


Figure 22: Micrographs of lapped cross section of the Core P-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm; and,

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint.

Scale bars are 1 mm.

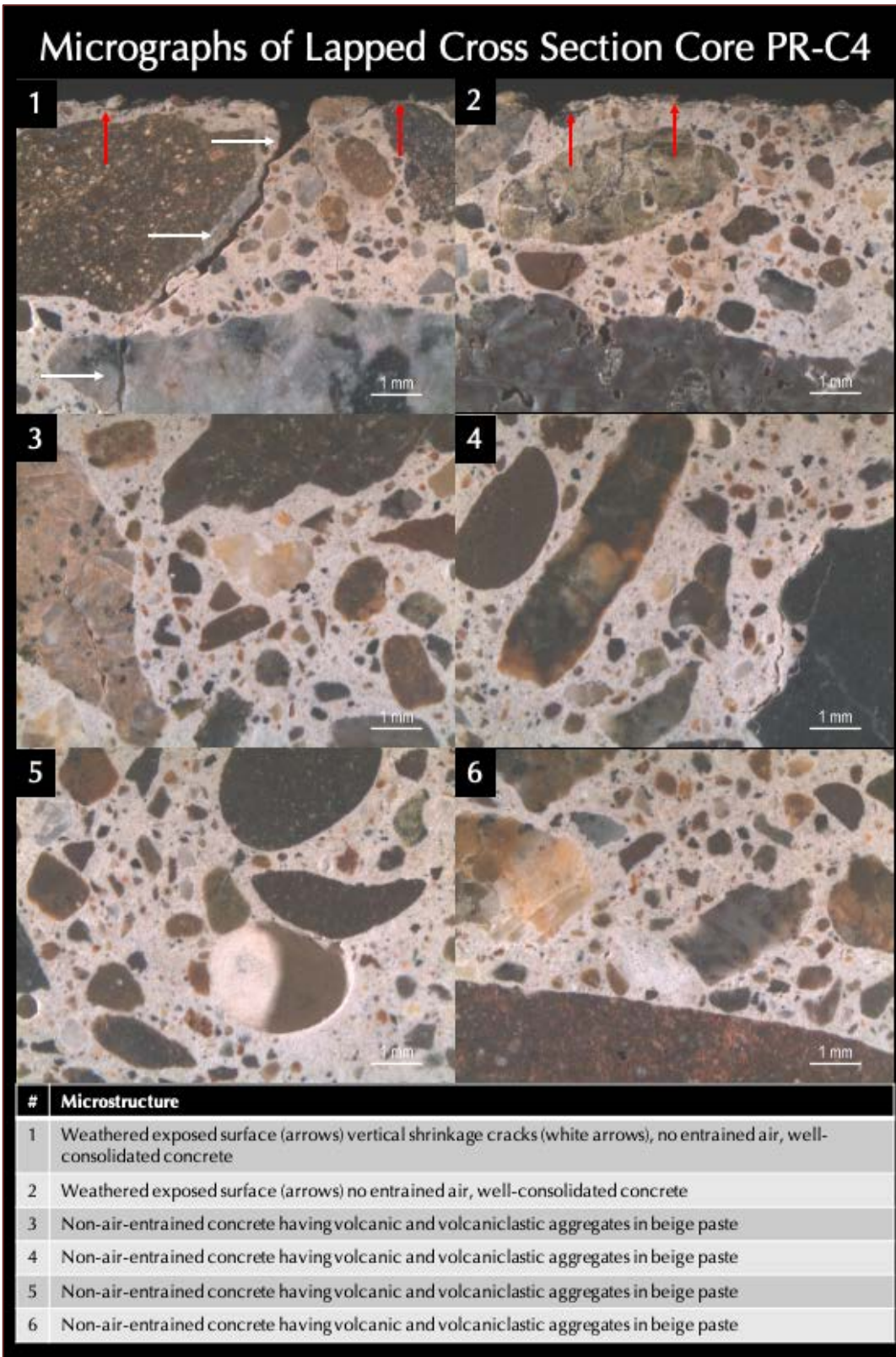


Figure 23: Micrographs of lapped cross section of the Core PR-C4 showing:

(a) The weathered exposed surface at the top;

(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

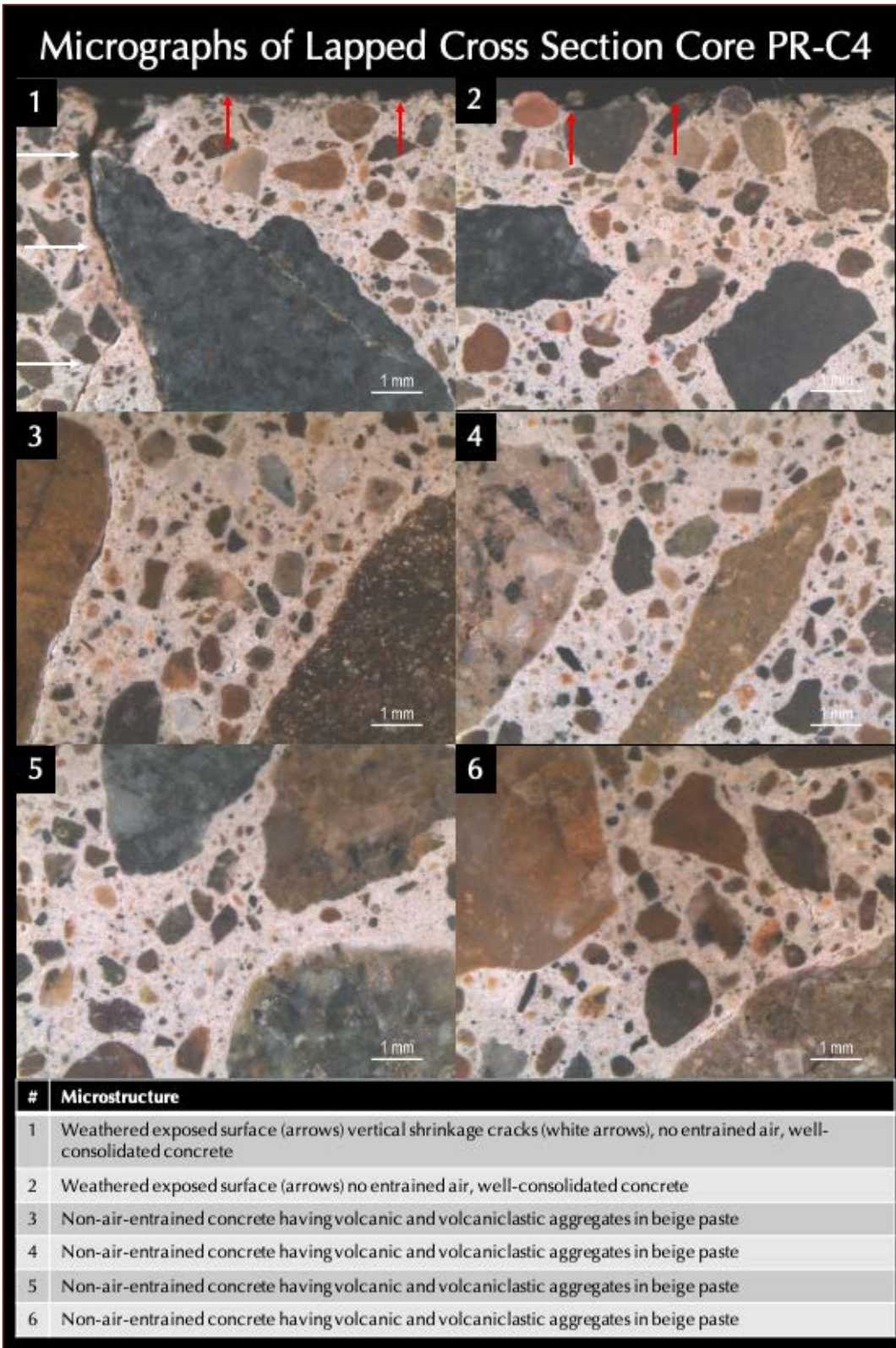


Figure 24: Micrographs of lapped cross section of the Core PR-C4 showing:

(a) The weathered exposed surface at the top;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

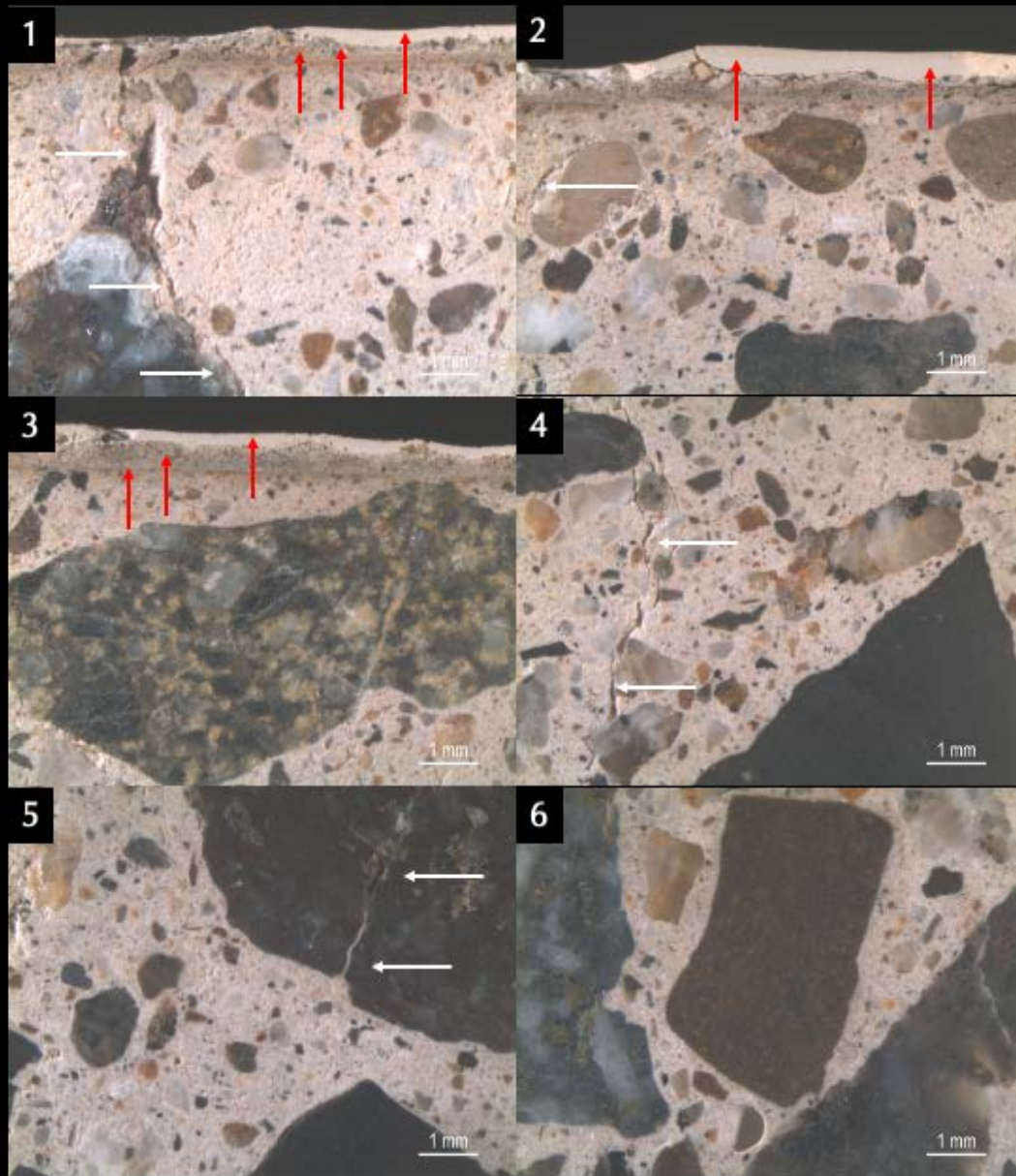
(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

Micrographs of Lapped Cross Section Core PS-C4



#	Microstructure
1	Multiple paint and cementitious coats (three red arrows) well-bonded to concrete, near-surface vertical shrinkage microcracks (white arrows), no entrained air, well-consolidated concrete
2	Same as #1
3	Same as #1 and 2
4	Vertical shrinkage microcracks (white arrows), no entrained air, well-consolidated concrete
5	Vertical shrinkage microcracks (white arrows), no entrained air, well-consolidated concrete
6	Non-air-entrained concrete having volcanic and volcanoclastic aggregates in beige paste

Figure 25: Micrographs of lapped cross section of the Core PS-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

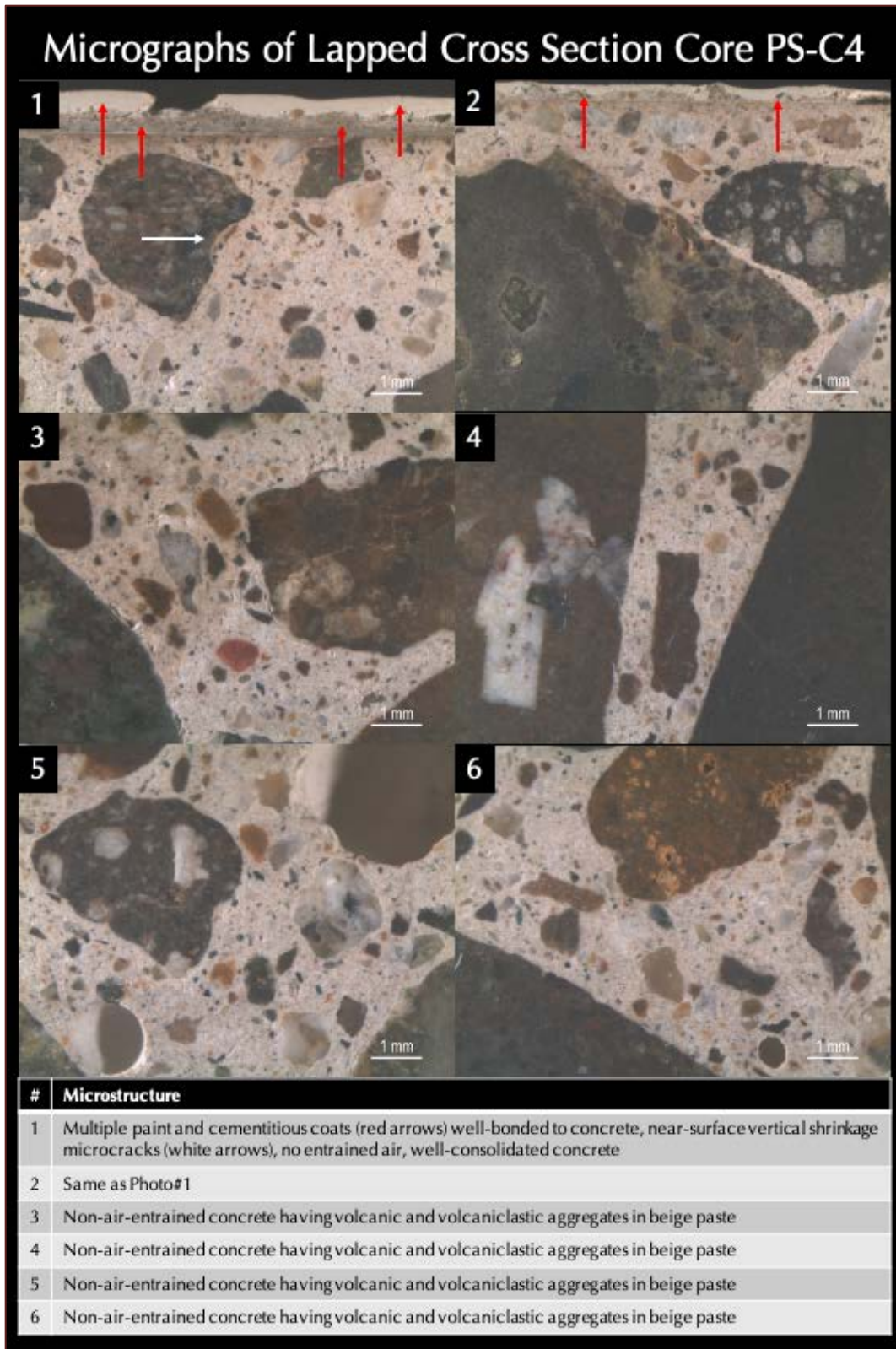


Figure 26: Micrographs of lapped cross section of the Core PS-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

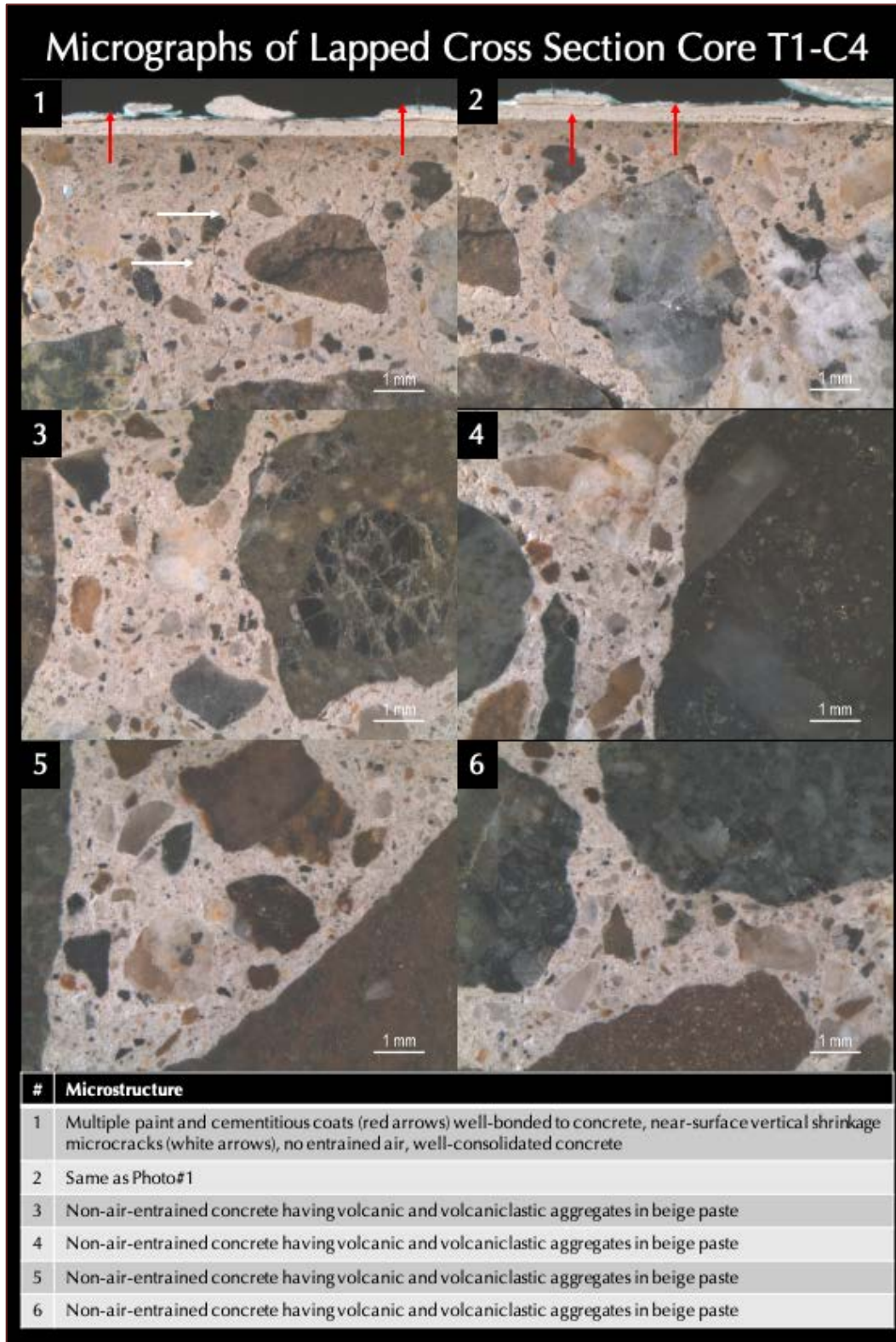


Figure 27: Micrographs of lapped cross section of the Core T1-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

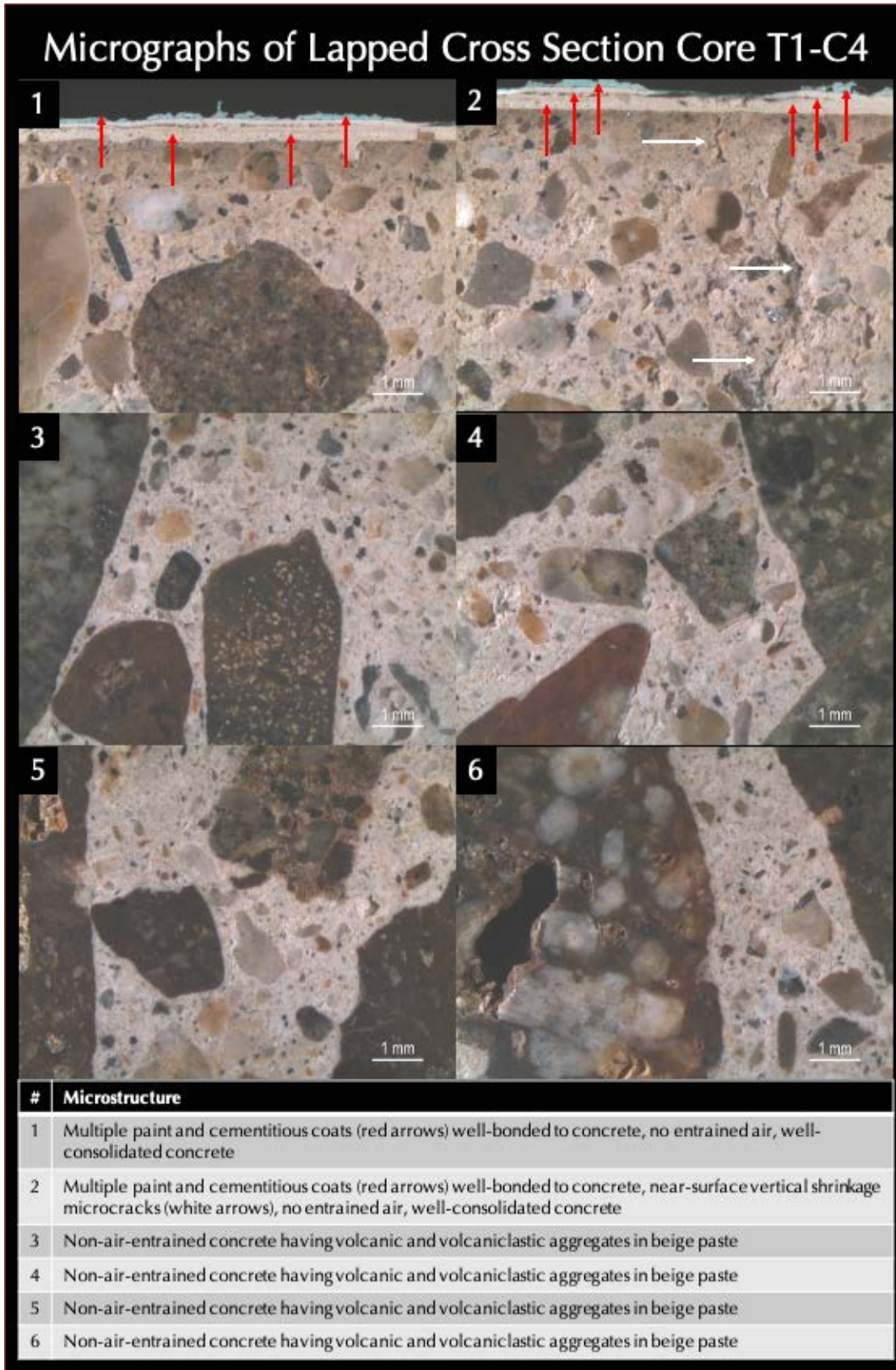


Figure 28: Micrographs of lapped cross section of the Core T1-C4 showing:

(a) Multiple layers of the protective paint coat (red arrows) at the top bonded to the main concrete body;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm;

(d) The top 1 mm zone of some surface alterations of concrete immediately beneath the paint; and,

(e) A few fine shrinkage microcracks at the top 10 to 15 mm of exposed surface are marked with white arrows.

Scale bars are 1 mm.

THIN SECTIONS

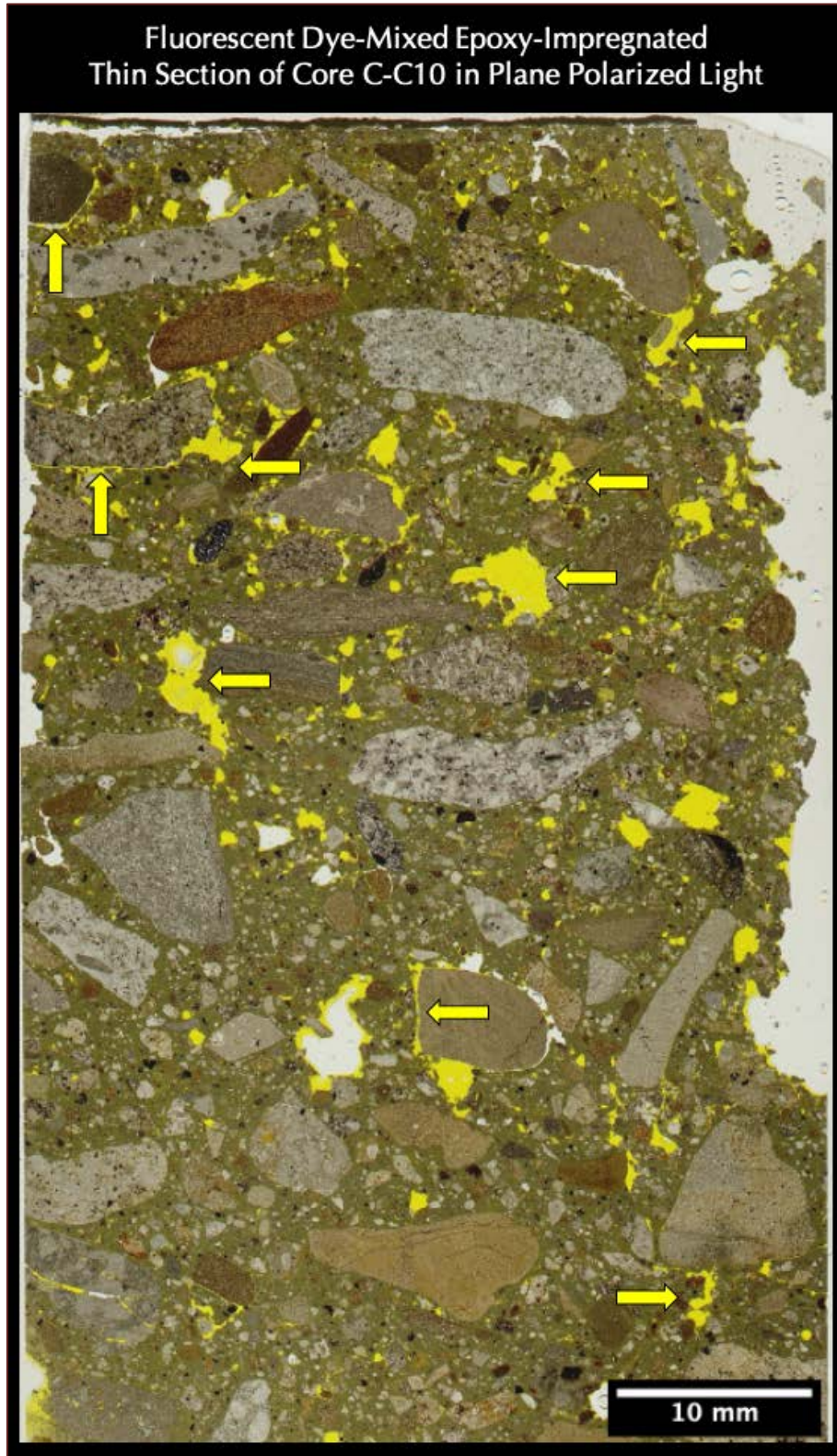


Figure 29: Fluorescent dye-mixed epoxy-impregnated thin section of Core C-C10 seen in the plane polarized light (PPL) mode by scanning the section in a film scanner with a polarizing filter showing:

(a) The paint coat having a nominal thickness of <1 mm; and,

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm, but many coarse, irregular-shaped voids and elongated entrapped voids that are highlighted in fluorescent epoxy; and,

(d) Some weak aggregate-paste bonds are marked by arrows.

**Fluorescent Dye-Mixed Epoxy-Impregnated
Thin Section of Core C-C10 in Crossed Polarized Light**

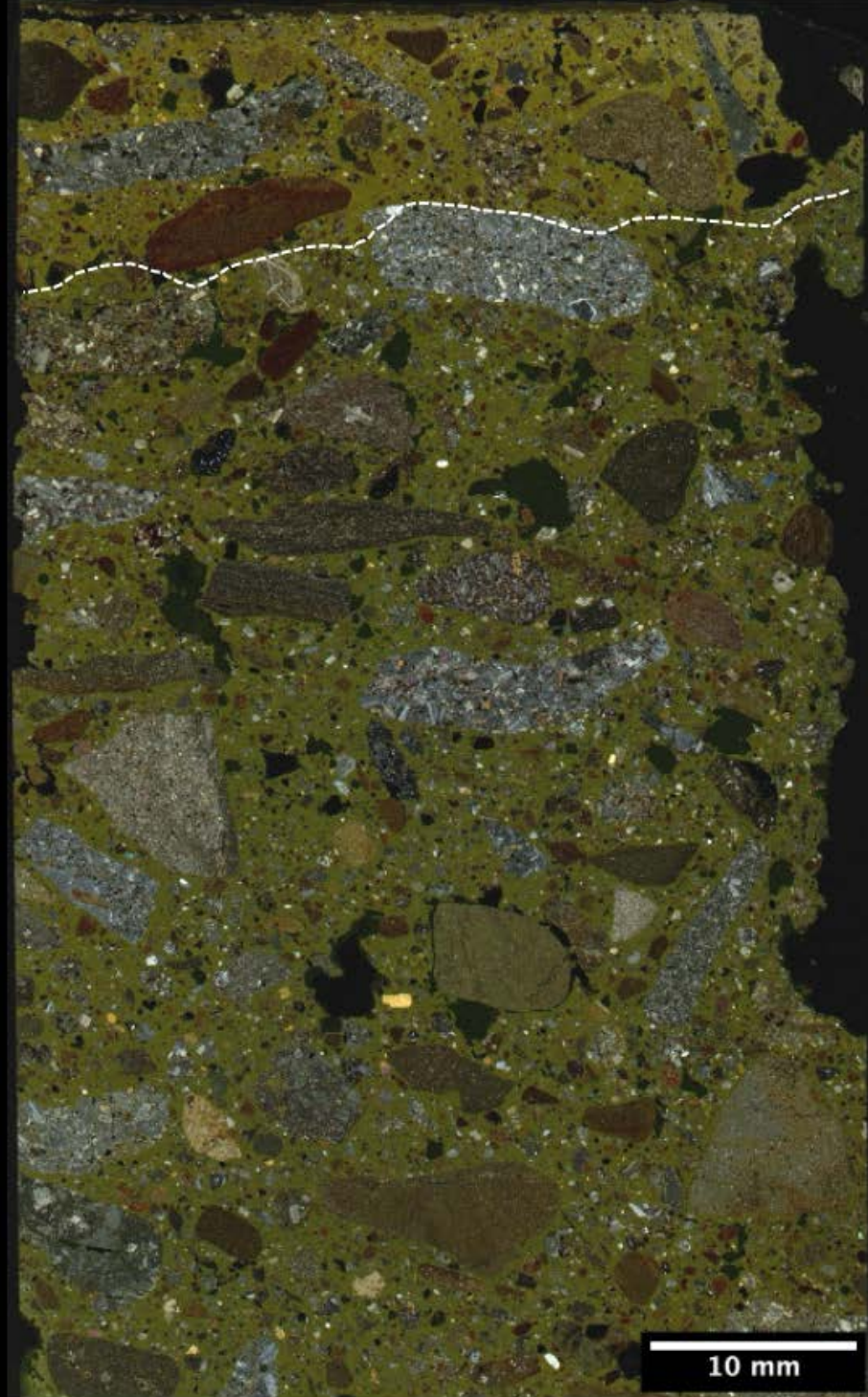


Figure 30: Fluorescent dye-mixed epoxy-impregnated thin section of Core C-C10 seen in the crossed polarized light (XPL) mode by scanning the section in a film scanner sandwiched between two polarizing filters at perpendicular positions showing:

(a) The carbonated paste at the top 10 to 15 mm separated from interior body by white dashed line, and,

(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste.

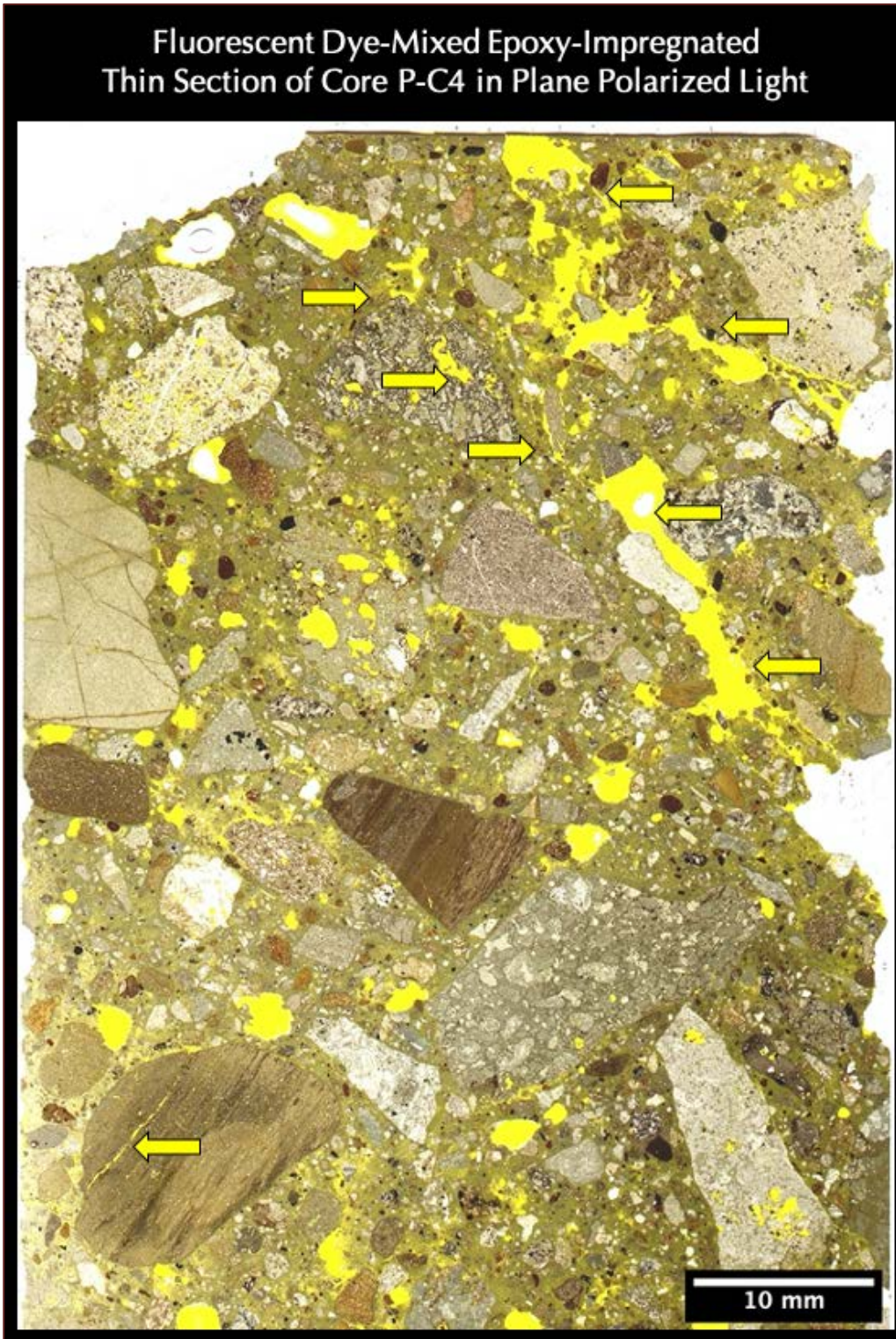


Figure 31: Fluorescent dye-mixed epoxy-impregnated thin section of Core P-C4 seen in the plane polarized light (PPL) mode by scanning the section in a film scanner with a polarizing filter showing:

(a) The paint coat having a nominal thickness of <1 mm;

(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm but many coarse, irregular-shaped voids and elongated entrapped voids that are highlighted in fluorescent epoxy; and,

(d) Some weak aggregate-paste bonds are marked by arrows.

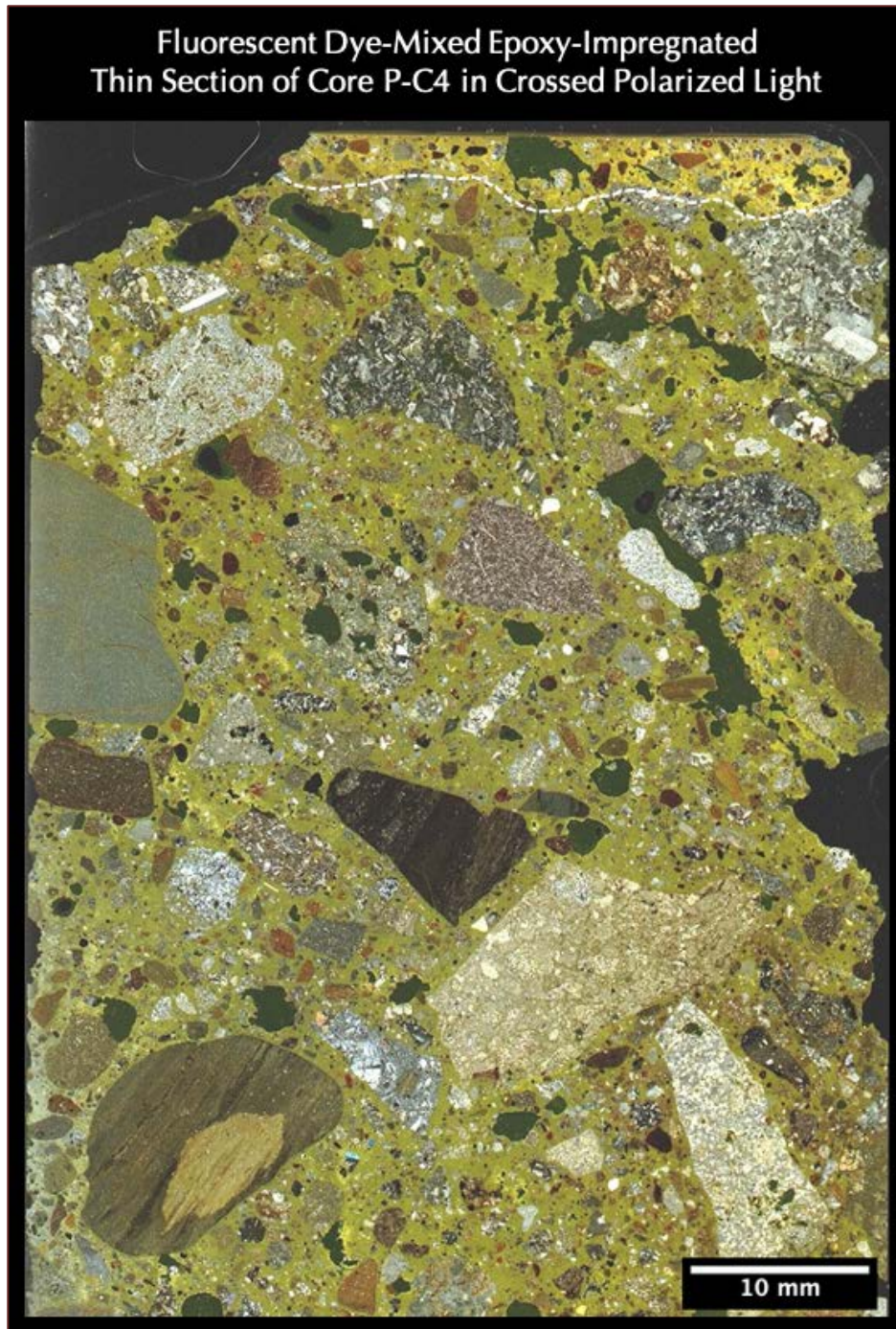


Figure 32: Fluorescent dye-mixed epoxy-impregnated thin section of Core P-C4 seen in the crossed polarized light (XPL) mode by scanning the section in a film scanner sandwiched between two polarizing filters at perpendicular positions showing:

(a) The carbonated paste at the top 10 to 15 mm separated from interior body by white dashed line; and,

(b) The main concrete body containing crushed volcanic and volcaniclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste.

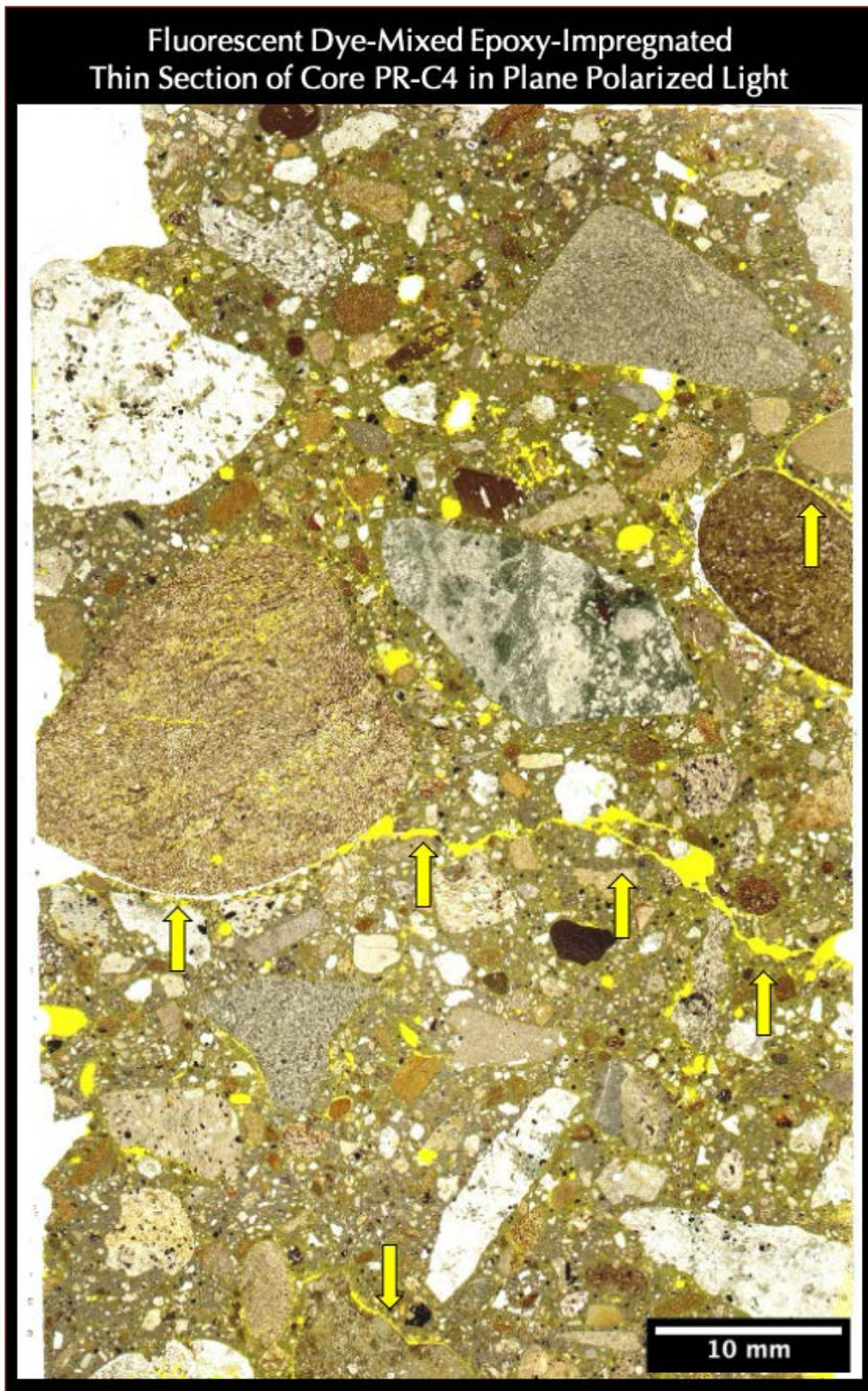


Figure 33: Fluorescent dye-mixed epoxy-impregnated thin section of Core PR-C4 seen in the plane polarized light (PPL) mode by scanning the section in a film scanner with a polarizing filter showing:

(a) The exposed surface region of concrete at the top,

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm, but many coarse, irregular-shaped voids and elongated entrapped voids that are highlighted in fluorescent epoxy; and,

(d) Some weak aggregate-paste bonds and a central crack are marked by arrows.



Figure 34: Fluorescent dye-mixed epoxy-impregnated thin section of Core PR-C4 seen in the crossed polarized light (XPL) mode by scanning the section in a film scanner sandwiched between two polarizing filters at perpendicular positions showing:

(a) The carbonated paste at the top 10 to 15 mm, and,

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste.

**Fluorescent Dye-Mixed Epoxy-Impregnated
Thin Section of Core PS-C4 in Plane Polarized Light**

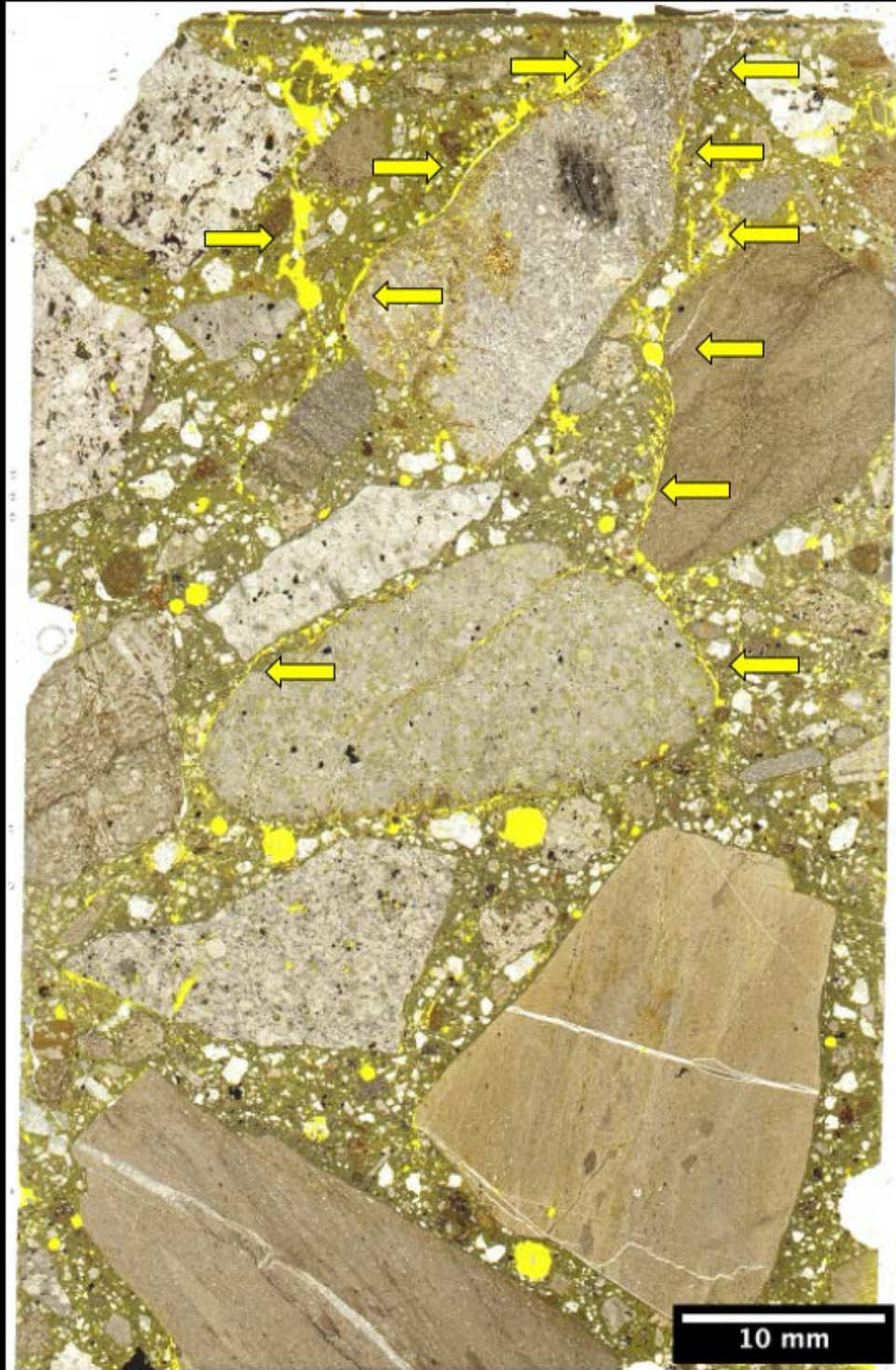


Figure 35: Fluorescent dye-mixed epoxy-impregnated thin section of Core PS-C4 seen in the plane polarized light (PPL) mode by scanning the section in a film scanner with a polarizing filter showing:

(a) The paint coat having a nominal thickness of <1 mm;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm, but many coarse, irregular-shaped voids and elongated entrapped voids that are highlighted in fluorescent epoxy; and,

(d) Some weak aggregate-paste bonds are marked by arrows.

**Fluorescent Dye-Mixed Epoxy-Impregnated
Thin Section of Core PS-C4 in Crossed Polarized Light**

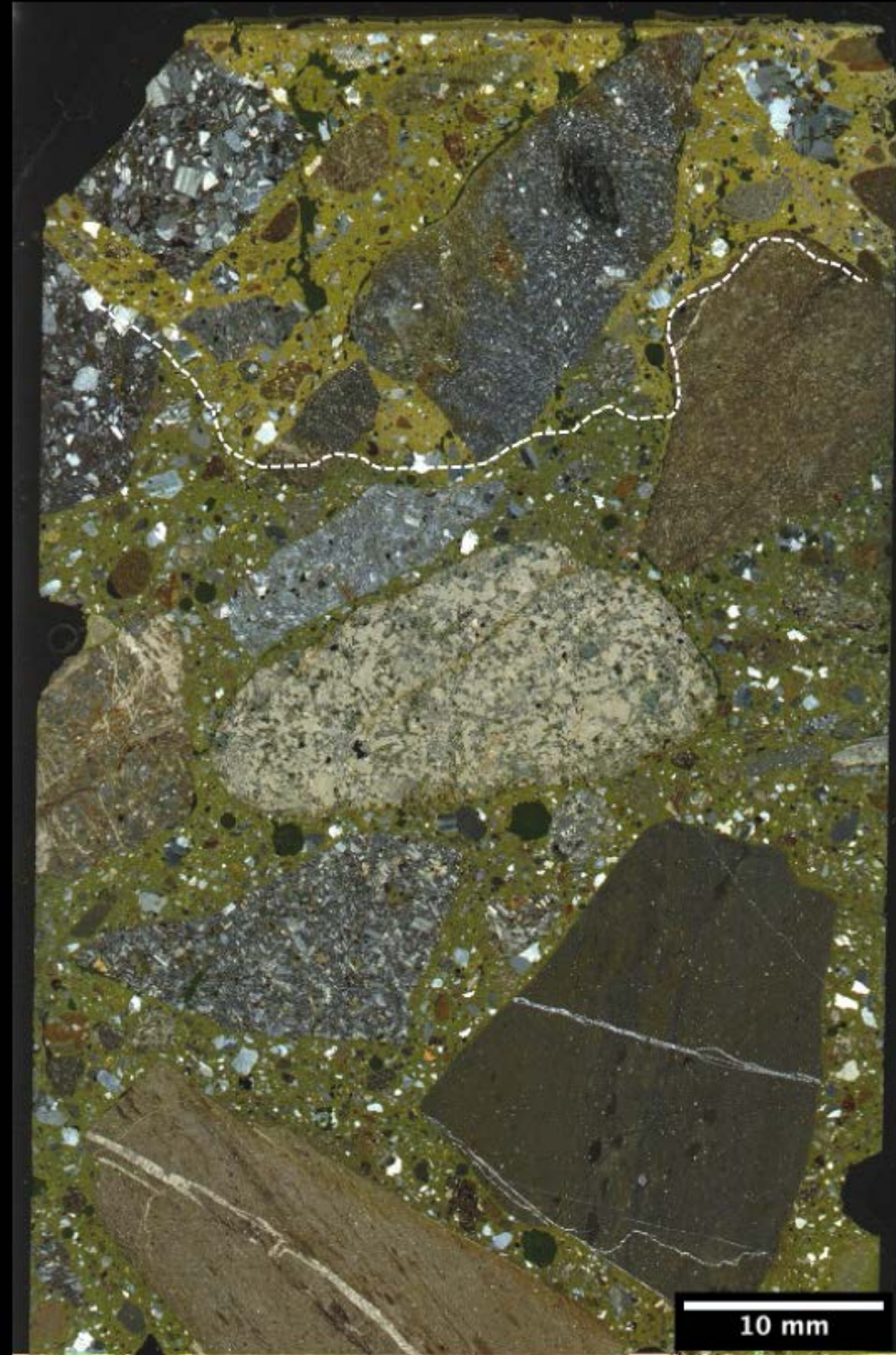


Figure 36: Fluorescent dye-mixed epoxy-impregnated thin section of Core PS-C4 seen in the crossed polarized light (XPL) mode by scanning the section in a film scanner sandwiched between two polarizing filters at perpendicular positions showing:

(a) The carbonated paste at the top 10 to 15 mm separated from interior body by white dashed line; and,

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste.

**Fluorescent Dye-Mixed Epoxy-Impregnated
Thin Section of Core T1-C4 in Plane Polarized Light**

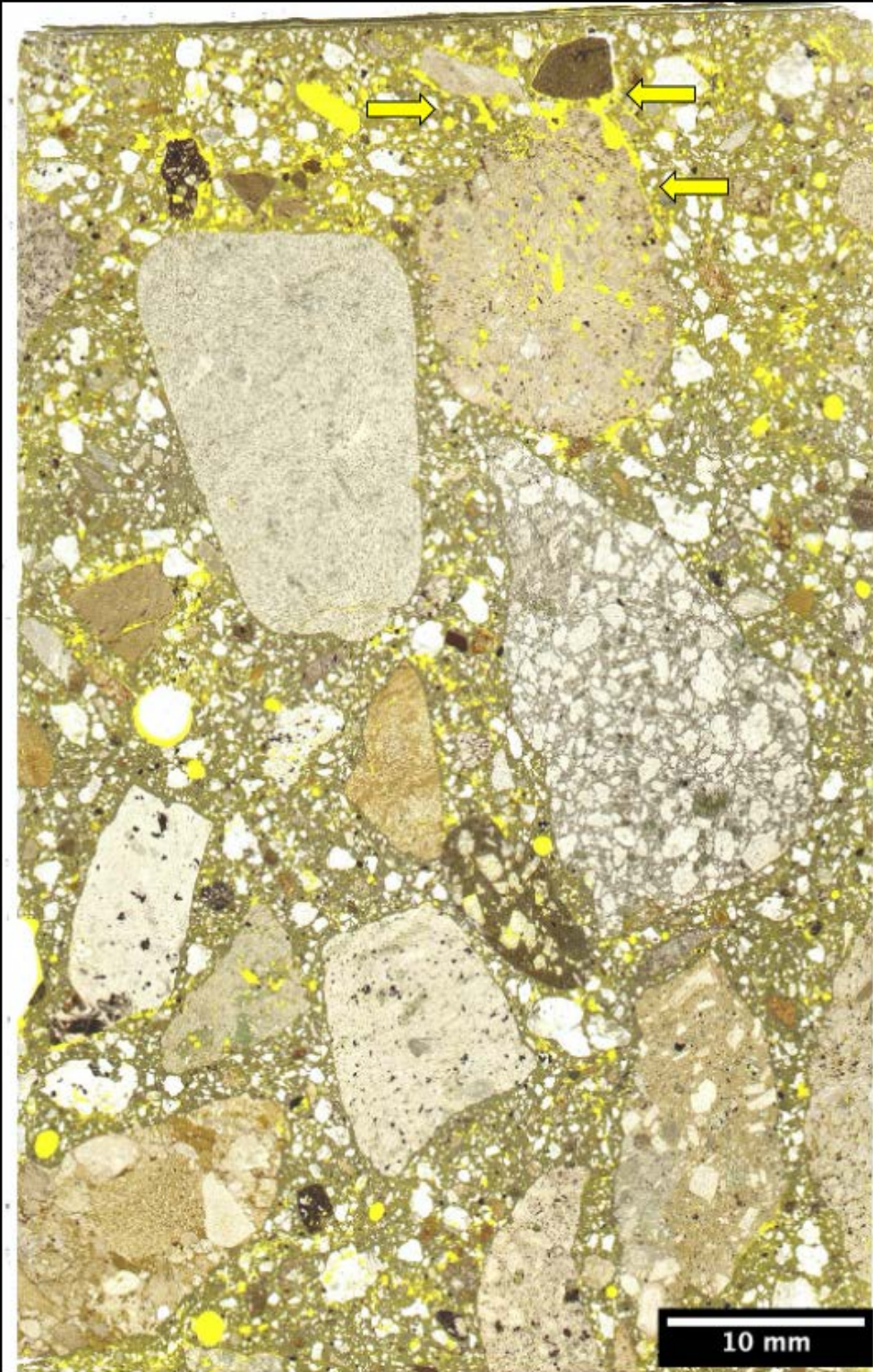


Figure 37: Fluorescent dye-mixed epoxy-impregnated thin section of Core T1-C4 seen in the plane polarized light (PPL) mode by scanning the section in a film scanner with a polarizing filter showing:

(a) The paint coat having a nominal thickness of <1 mm;

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste;

(c) The non-air-entrained nature of the concrete due to the lack of any fine, discrete, spherical and near-spherical entrained air voids of sizes less than 1 mm, but many coarse, irregular-shaped voids and elongated entrapped voids that are highlighted in fluorescent epoxy; and,

(d) Some elongated stringy voids at the surface region are marked by arrows.

**Fluorescent Dye-Mixed Epoxy-Impregnated
Thin Section of Core T1-C4 in Crossed Polarized Light**

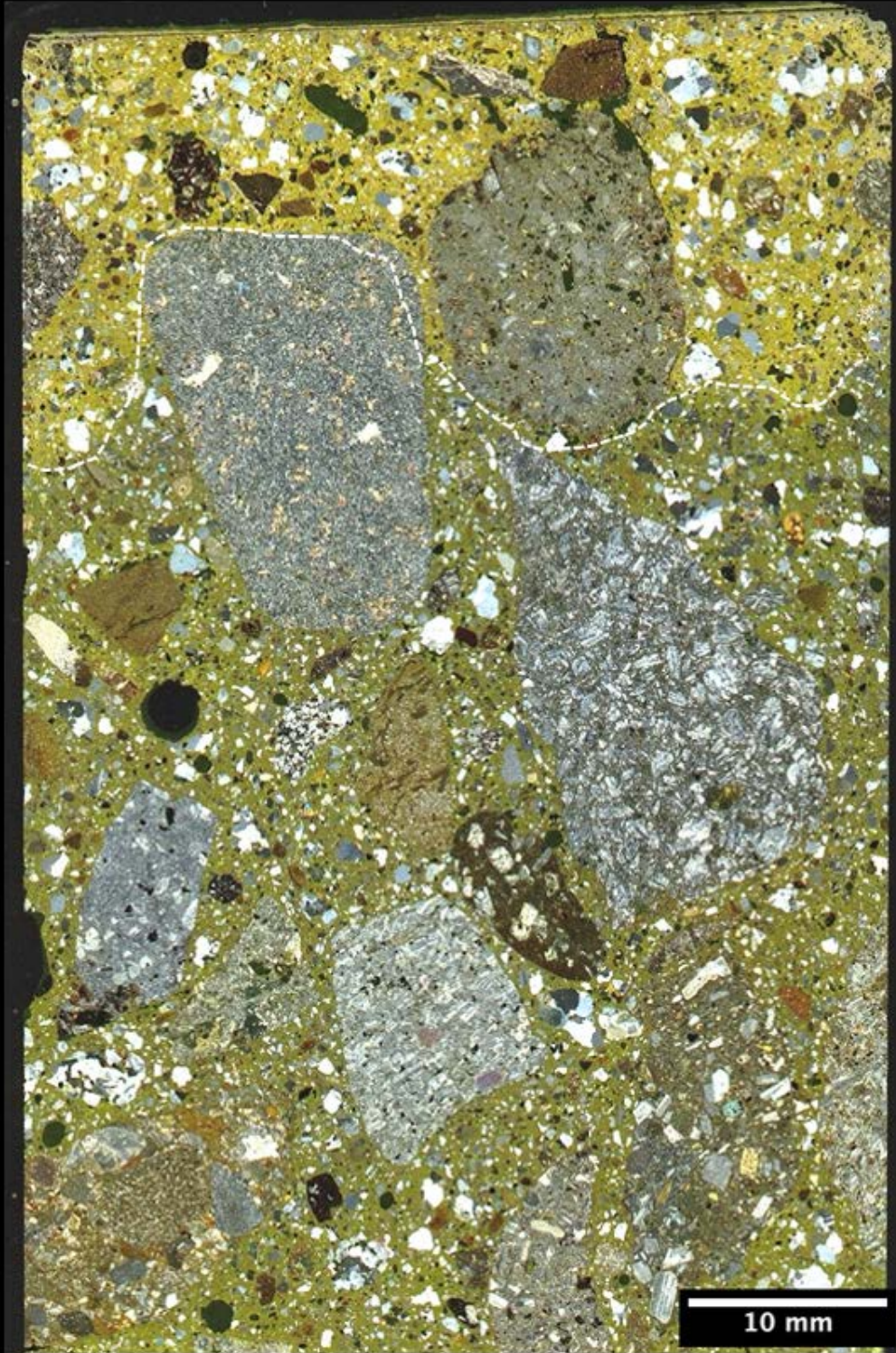


Figure 38: Fluorescent dye-mixed epoxy-impregnated thin section of Core T1-C4 seen in the crossed polarized light (XPL) mode by scanning the section in a film scanner sandwiched between two polarizing filters at perpendicular positions showing:

(a) The carbonated paste at the top 10 to 15 mm separated from interior body by white dashed line, and,

(b) The main concrete body containing crushed volcanic and volcanoclastic gravel coarse aggregate where aggregate particles are subrounded to subangular, dense, variably colored, well-graded, and well-distributed, natural siliceous sand and finer fractions of volcanic rocks and minerals in fine aggregate, all dispersed in a Portland cement paste.

MICROGRAPHS OF THIN SECTIONS

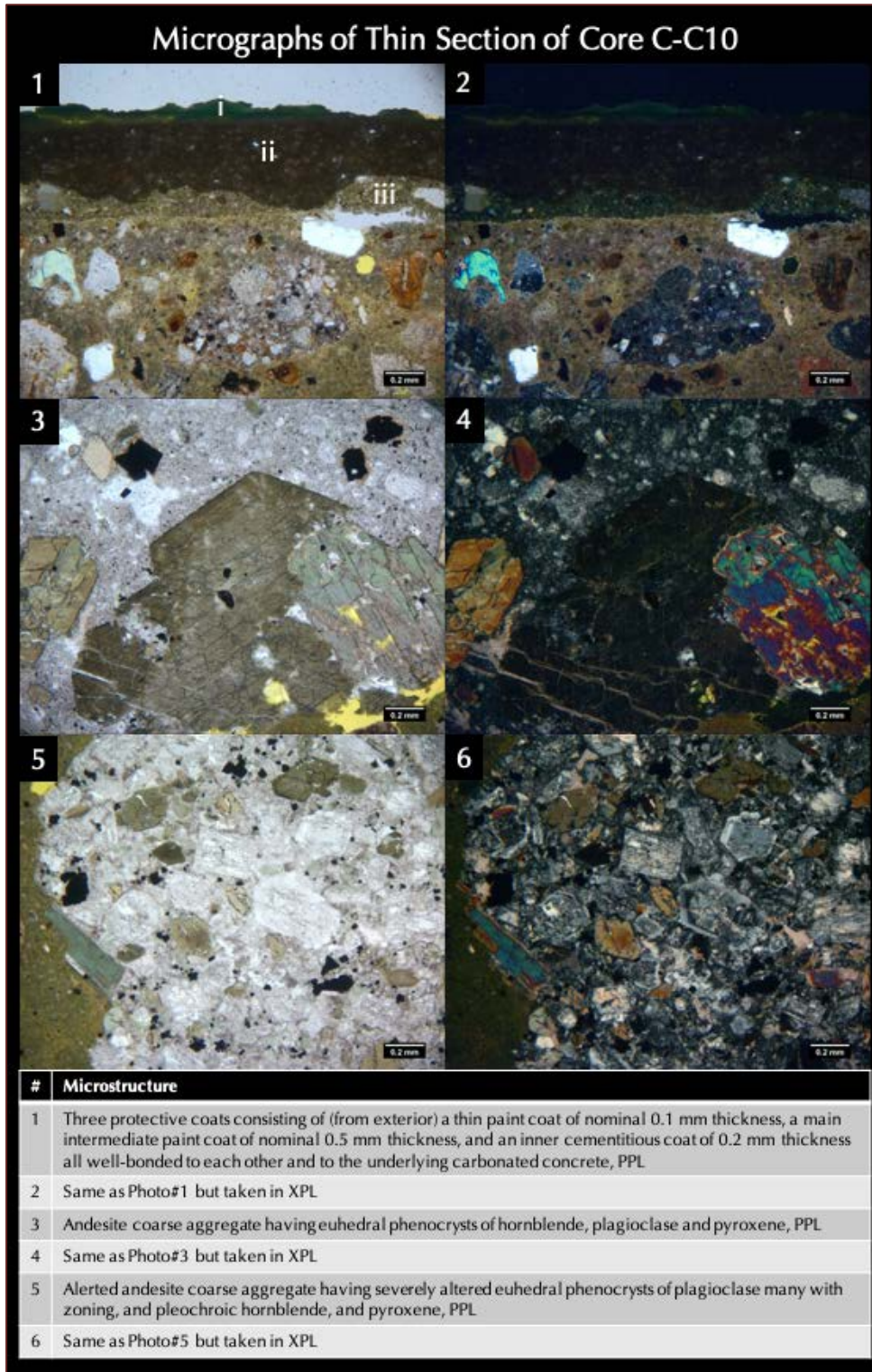


Figure 39: Micrographs of thin section of Core C-C10 showing:

(a) The protective paint coats separated into three distinct layers of applications marked as i to iii in top left photo,

(b) The main concrete body containing crushed gravel volcanic and volcanoclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan; and,

(c) The carbonated surface region of concrete in the top two photos.

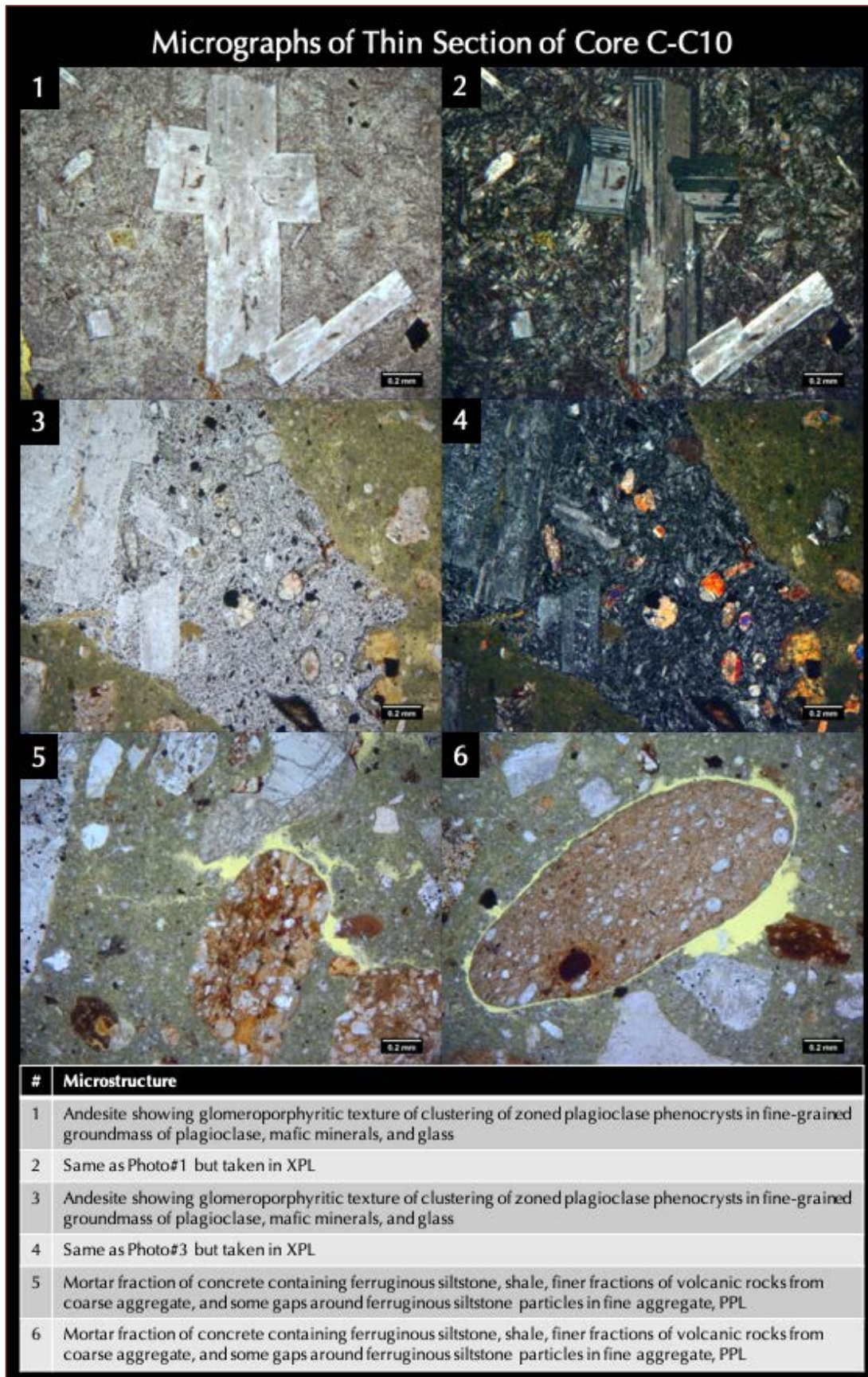


Figure 40: Micrographs of thin section of Core C-C10 showing:

(a) Crushed gravel volcanic and volcaniclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan,

(b) Glomeroporphyritic texture of plagioclase phenocrysts in andesite in the top and middle row photos; and,

(c) Some weak aggregate-paste bonds with gaps highlighted by fluorescent epoxy in the bottom row photos.

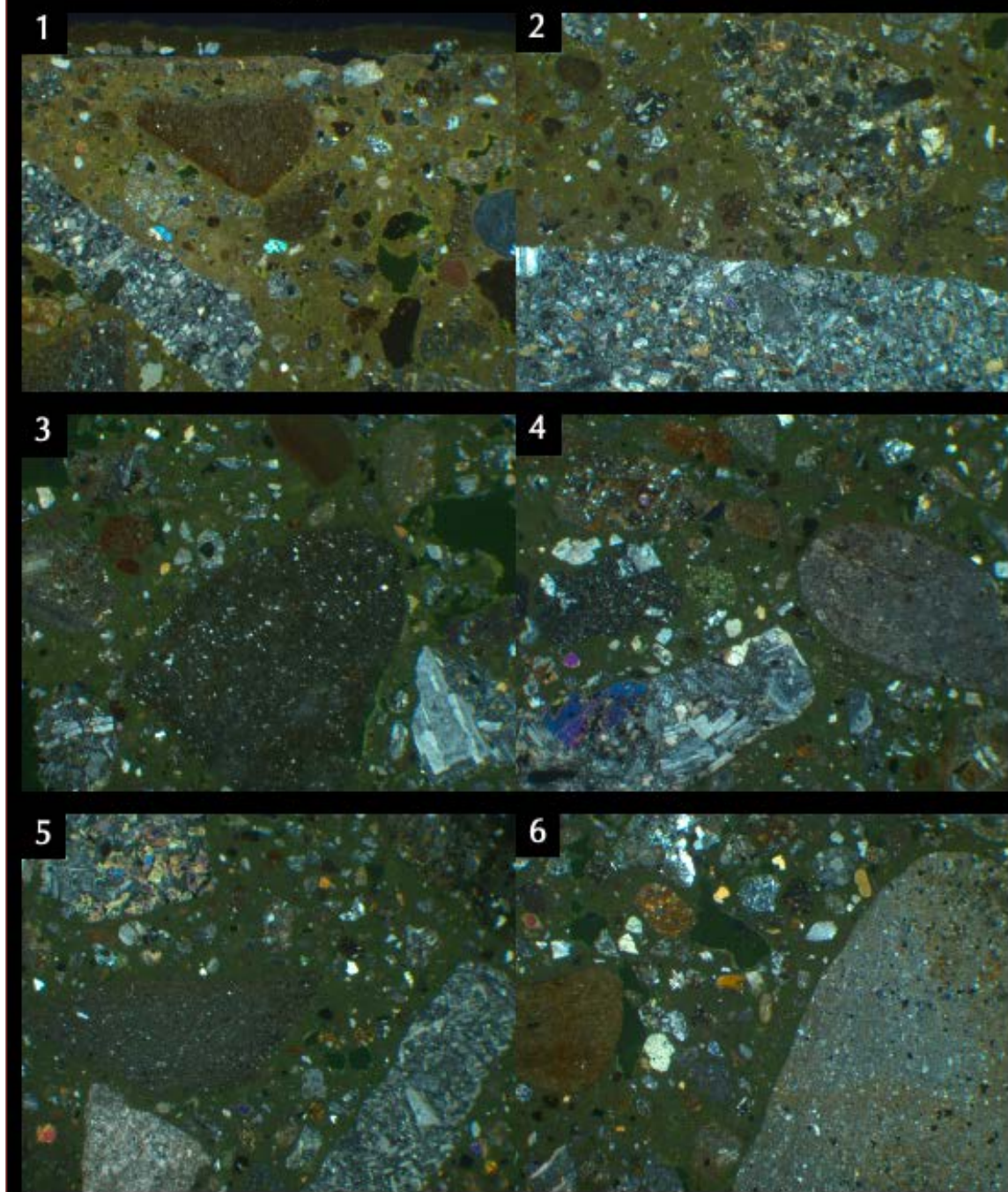
Micrographs of Thin Section of Core C-C10

Figure 41: Micrographs of thin section of Core C-C10 showing:

(a) The protective paint coats in the top left photo,

(b) The main concrete body containing crushed gravel volcanic and volcanoclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan; and,

(c) The carbonated surface region of concrete in the top left photo.



#	Microstructure
1	Carbonated exposed surface region of concrete containing mixed silica sand and finer fractions of volcanic rocks of coarse aggregate, XPL
2	Carbonated exposed surface region of concrete containing mixed silica sand and finer fractions of volcanic rocks of coarse aggregate, an andesite coarse aggregate at the bottom part of photo, XPL
3 to 6	Interior concrete containing various siliceous, argillaceous, volcanic, and volcanoclastic particles of aggregates in a Portland cement paste, XPL

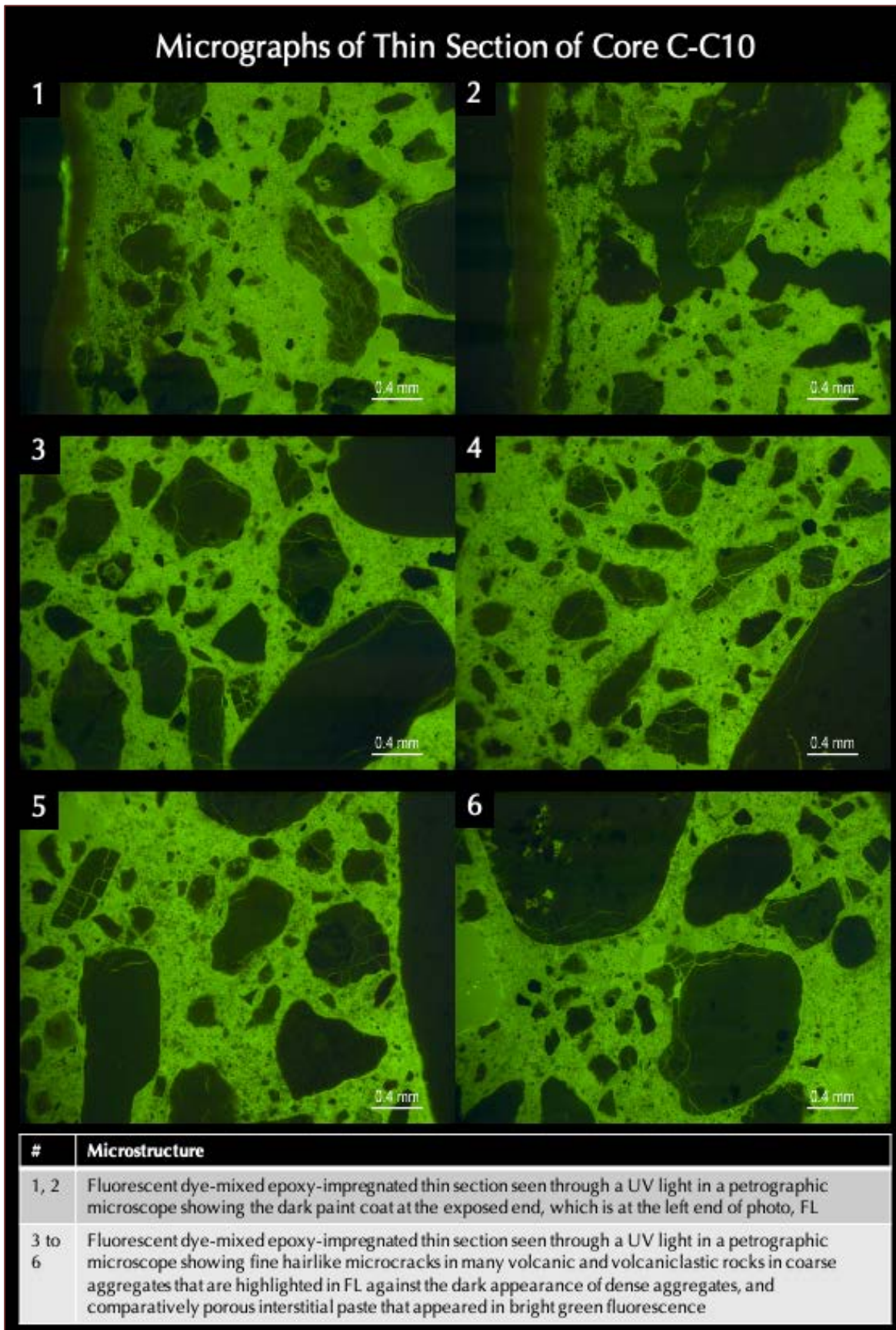


Figure 42: Micrographs of fluorescent dye-mixed epoxy-impregnated thin section of Core C-C10 in UV light showing:

- (a) The protective paint coats at the left sides of top two photos,
- (b) The main concrete body having relatively porous Portland cement paste that is highlighted in UV fluorescence whereas
- (c) Dense aggregate particles that appeared dark in UV light except
- (d) Some fine, hairline microcracks in aggregate particles that are highlighted in UV light (the purpose of this observation is to highlight those fine microcracks in aggregate particles).

Micrographs of Thin Section of Core P-C4

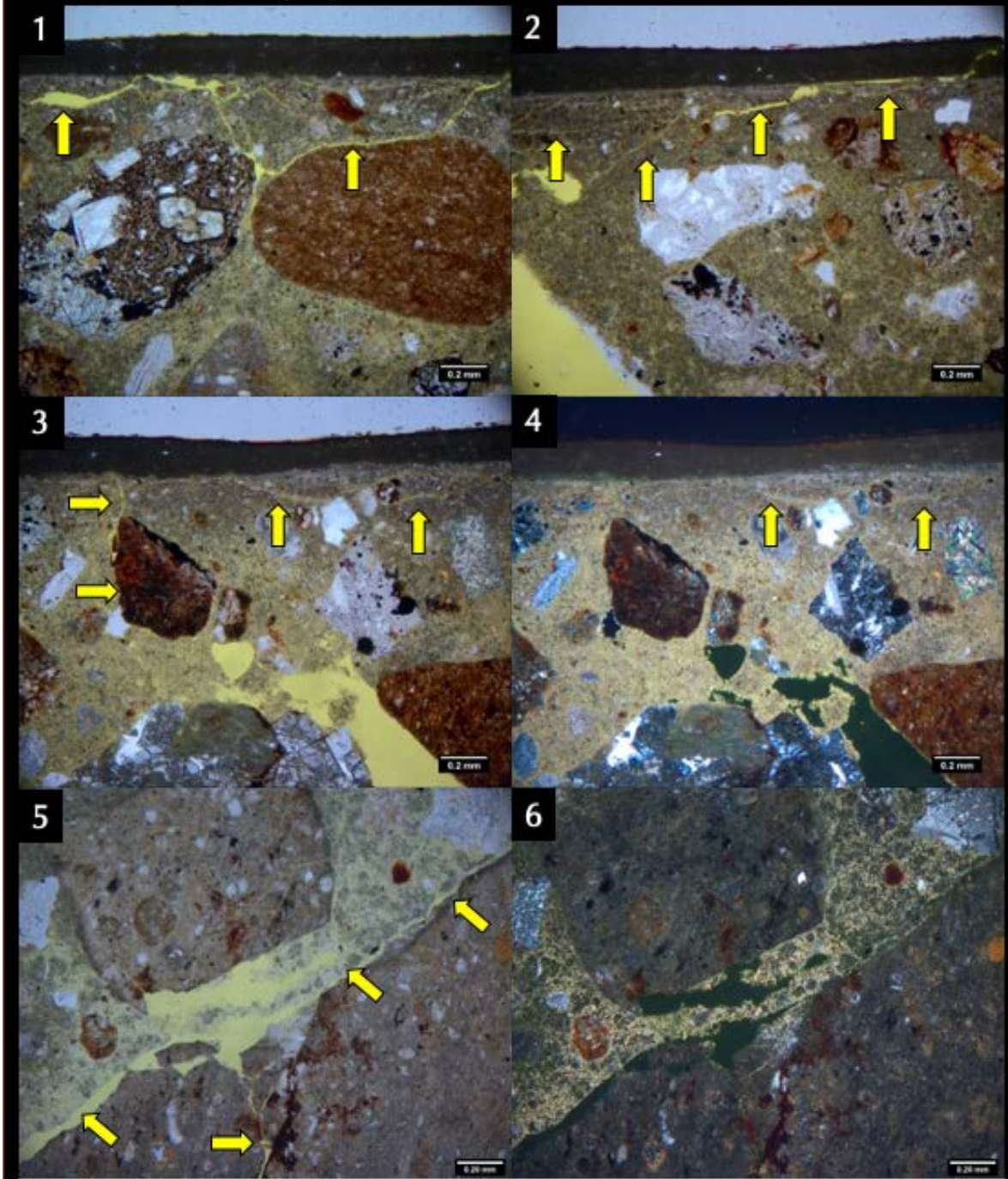


Figure 43: Micrographs of thin section of Core P-C4 showing:

(a) The protective paint coats,

(b) The main concrete body containing crushed gravel volcanic and volcanoclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan, and,

(c) The carbonated surface region of concrete.

Arrows mark the fine hairline microcracks in concrete.

#	Microstructure
1	Protective paint coat well-bonded to concrete. Immediately beneath the paint, near-surface region of concrete showed surface-parallel and perpendicular shrinkage microcracks marked by arrows.
4	Ferruginous shale, and andesitic volcanic rock particles in aggregates, PPL and XPL
5	Two fine-grained (aphanitic) predominantly glassy volcanic rock particles in coarse aggregate with microcracks along aggregate-paste interfaces marked by arrows
6	Same as Photo# 5 in XPL

Micrographs of Thin Section of Core P-C4

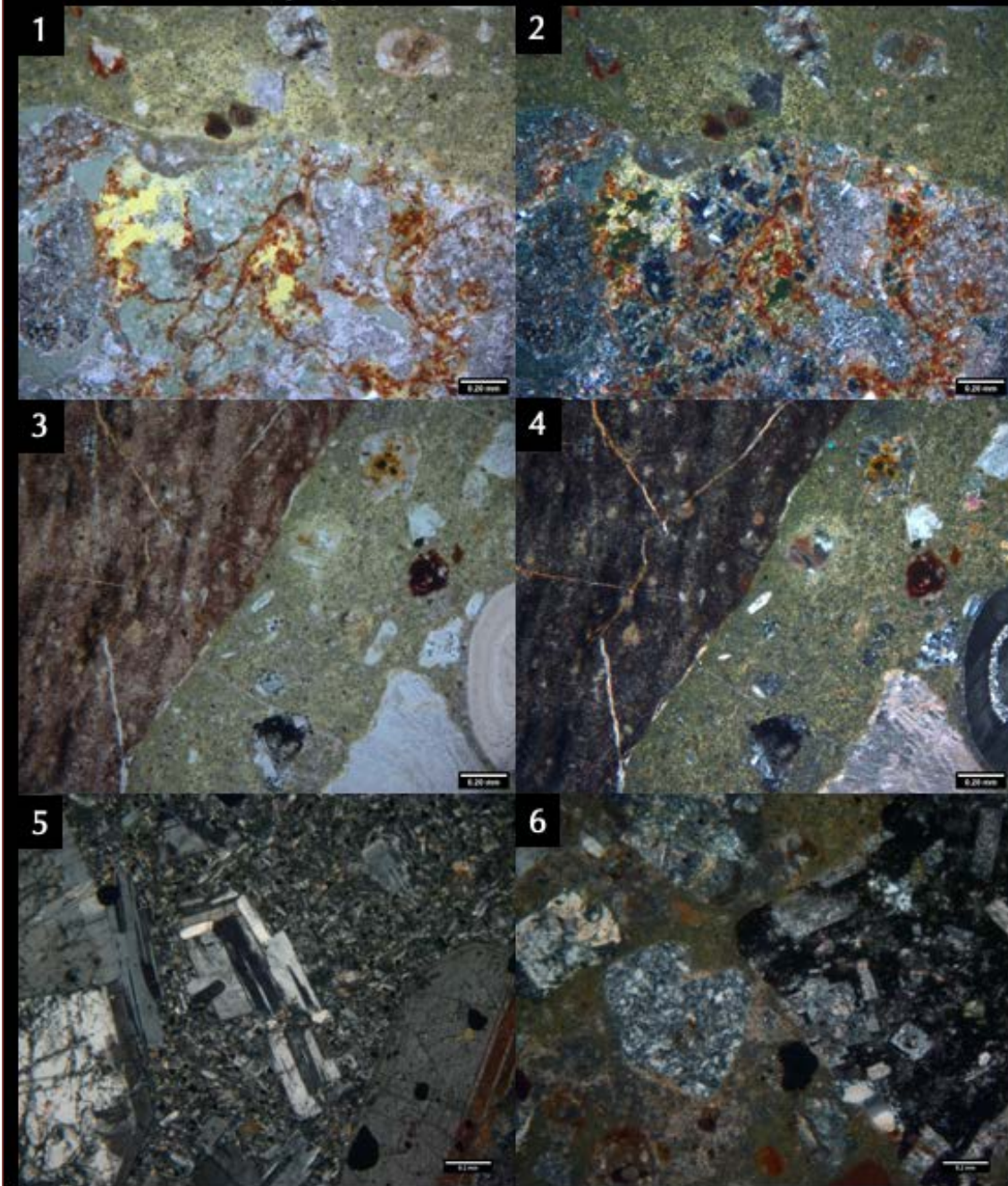


Figure 44: Micrographs of thin section of Core P-C4 showing:

(a) crushed gravel volcanic and volcaniclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan;

(b) Glassy volcanic rock particles showing reddish-brown color in PPL and darker near-isotropic color in XPL in the middle row, and,

(c) Plagioclase phenocrysts in andesitic volcanic rock particle in the bottom left photo.

#	Microstructure
1	Oxidation, alteration, and internal cracking in the volcaniclastic rock of coarse aggregate, PPL
2	Same as Photo#1 but taken in XPL
3	Ferruginous and fine-grained (aphanitic) mostly glassy volcanic rock coarse aggregate, seashell and finer fraction of volcanic rocks in fine aggregate and interstitial carbonated Portland cement paste, PPL
4	Same as Photo#3 but taken in XPL
5,	Andesitic volcanic rock in coarse aggregate containing lath-shaped euhedral to subhedral phenocrysts of plagioclase in finer-grained groundmass of plagioclase, pyroxene, glass, and opaque
6	

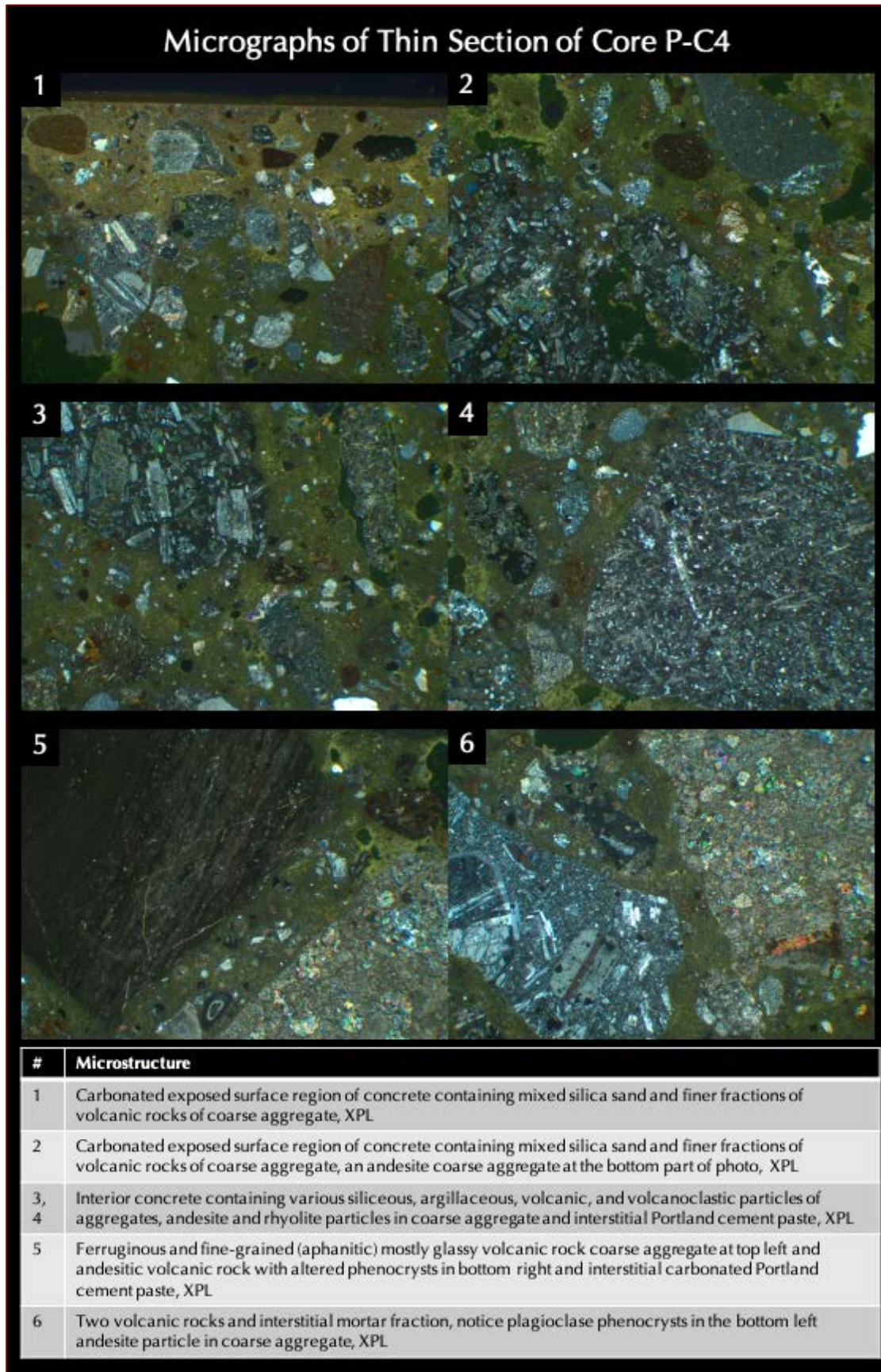


Figure 45: Micrographs of thin section of Core P-C4 showing crushed gravel volcanic and volcanoclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

Micrographs of Thin Section of Core P-C4

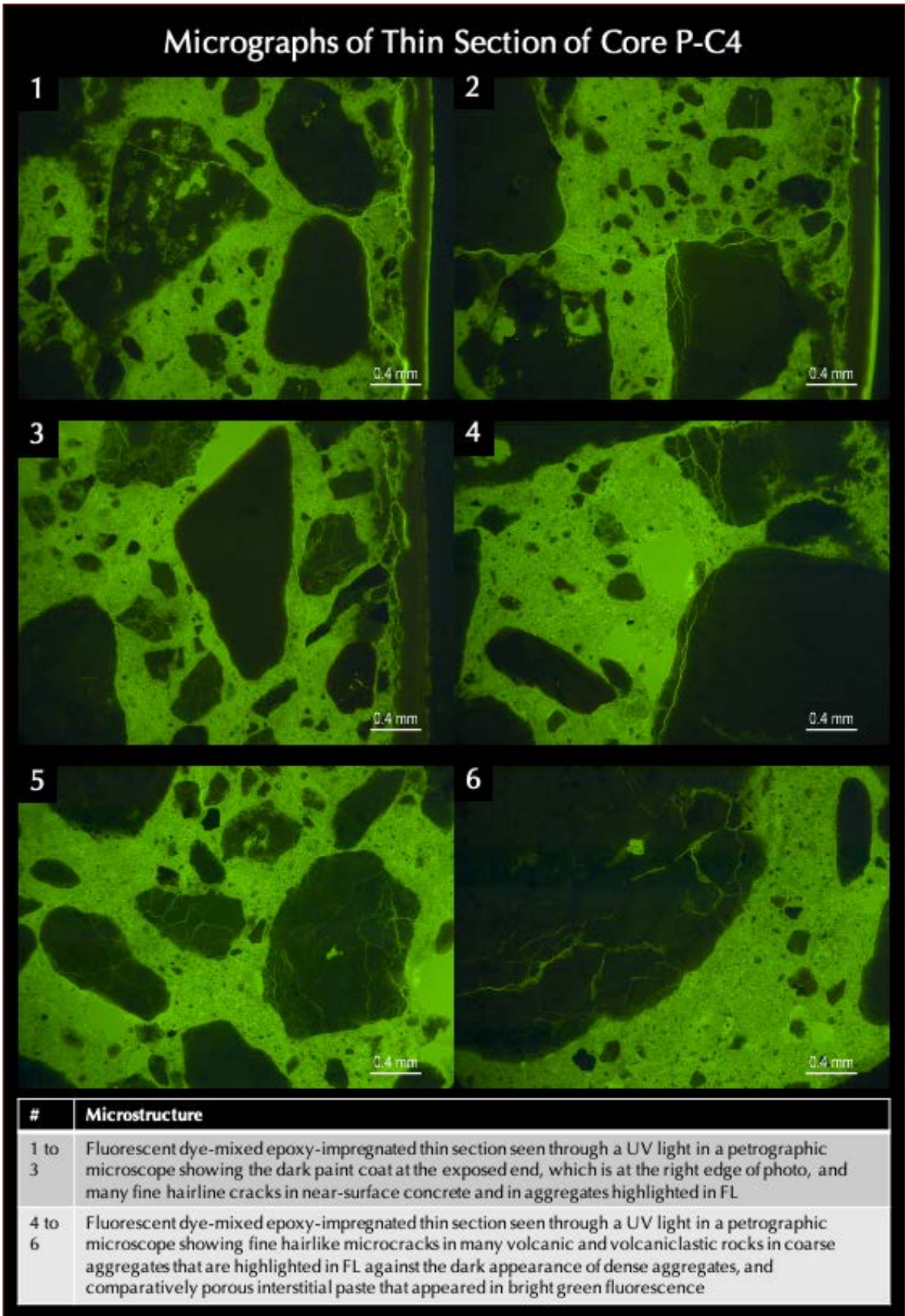
Figure 46: Micrographs of fluorescent dye-mixed epoxy-impregnated thin section of Core P-C4 in UV light showing:

(a) The protective paint coats at the right sides of top two photos,

(b) The main concrete body having relatively porous Portland cement paste that is highlighted in UV fluorescence whereas

(c) Dense aggregate particles that appeared dark in UV light except

(d) Some fine, hairline microcracks in aggregate particles that are highlighted in UV light (the purpose of this observation is to highlight those fine microcracks in aggregate particles).



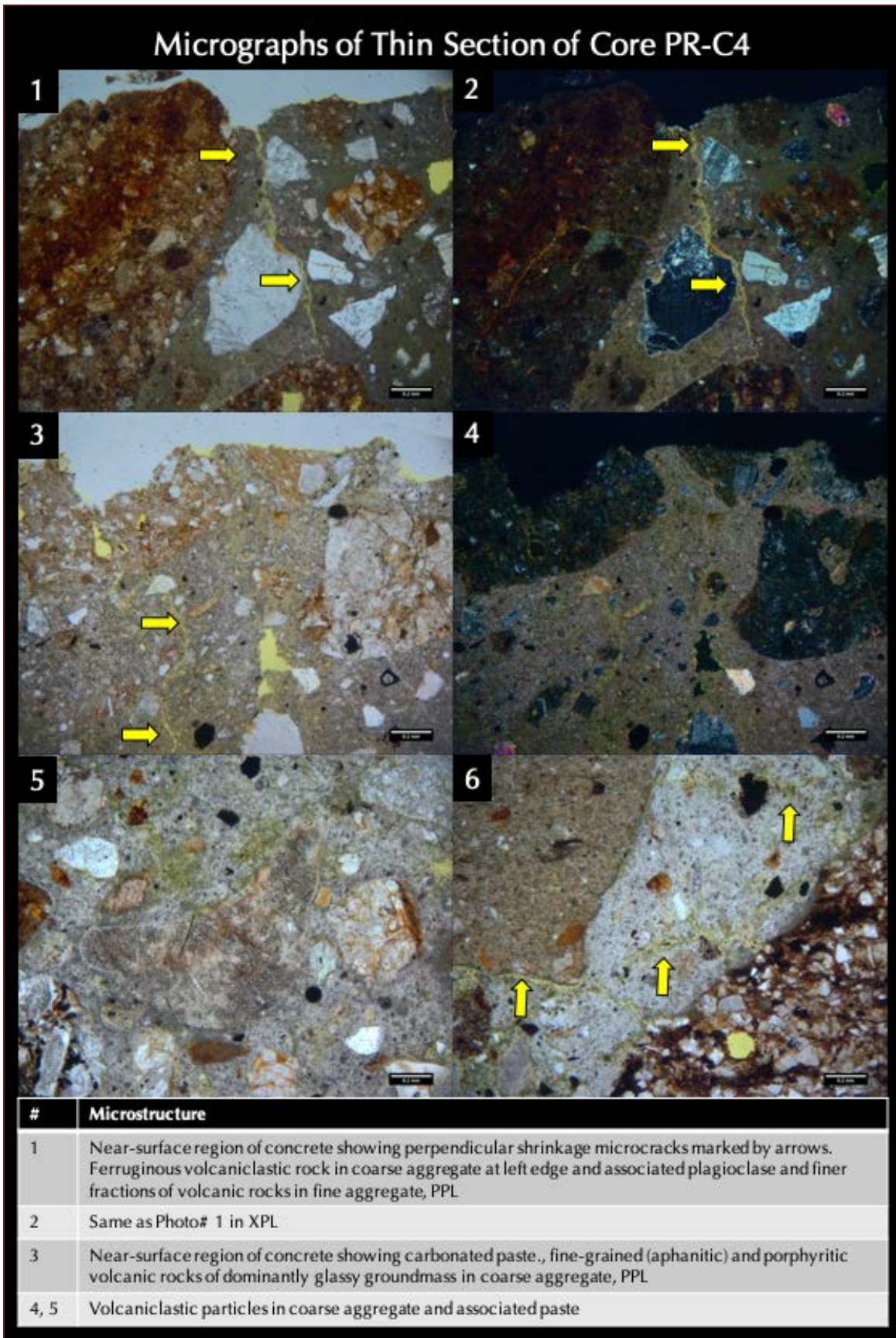


Figure 47: Micrographs of thin section of Core PR-C4 showing:

(a) The weathered exposed surface region with vertical shrinkage microcrack in the top row;

(b) The main concrete body containing crushed gravel volcanic and volcaniclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan, and,

(c) The carbonated surface region of concrete.

Arrows the mark the fine hairline microcracks in concrete.

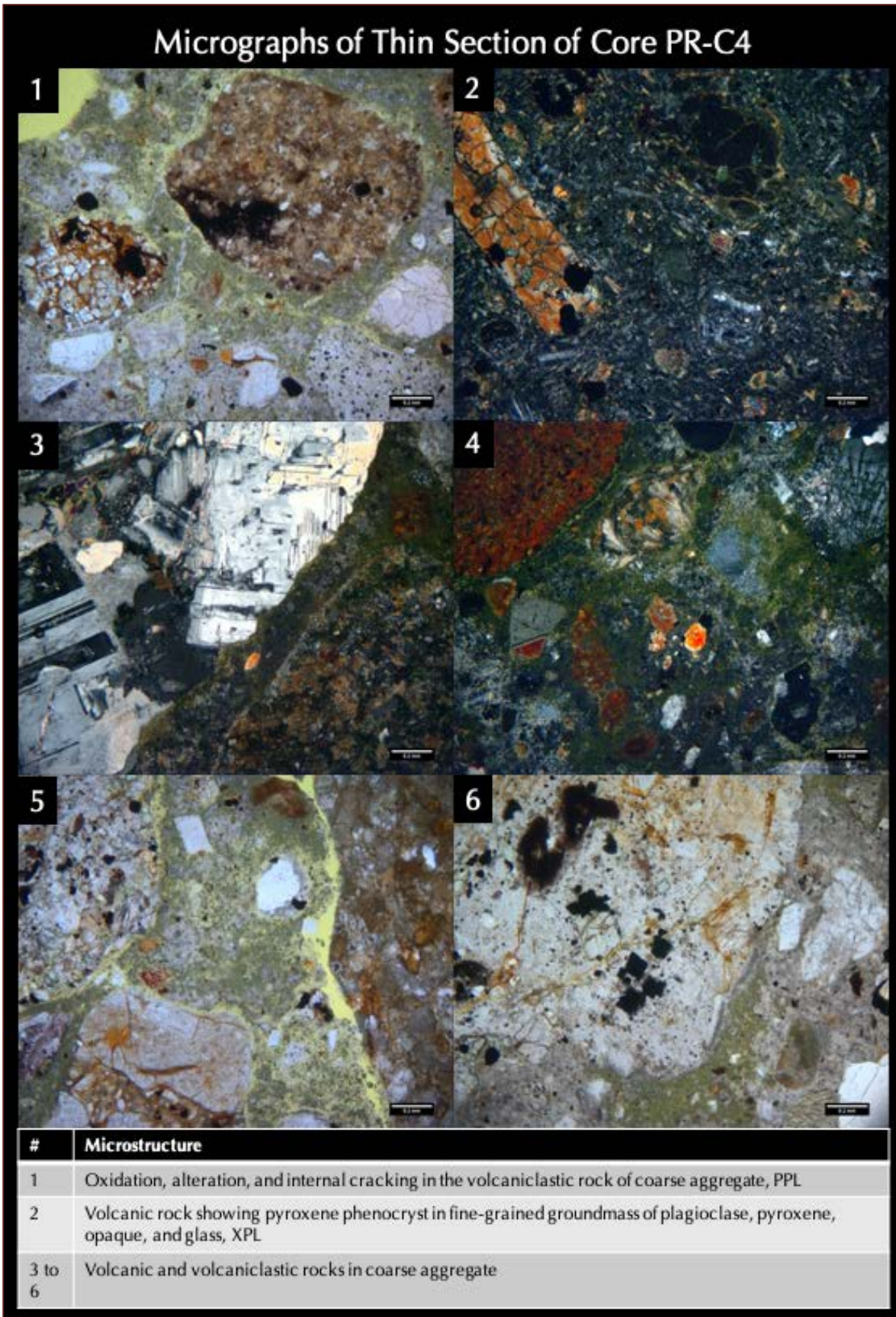


Figure 48: Micrographs of thin section of Core PR-C4 showing crushed gravel volcanic and volcaniclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

Micrographs of Thin Section of Core PR-C4

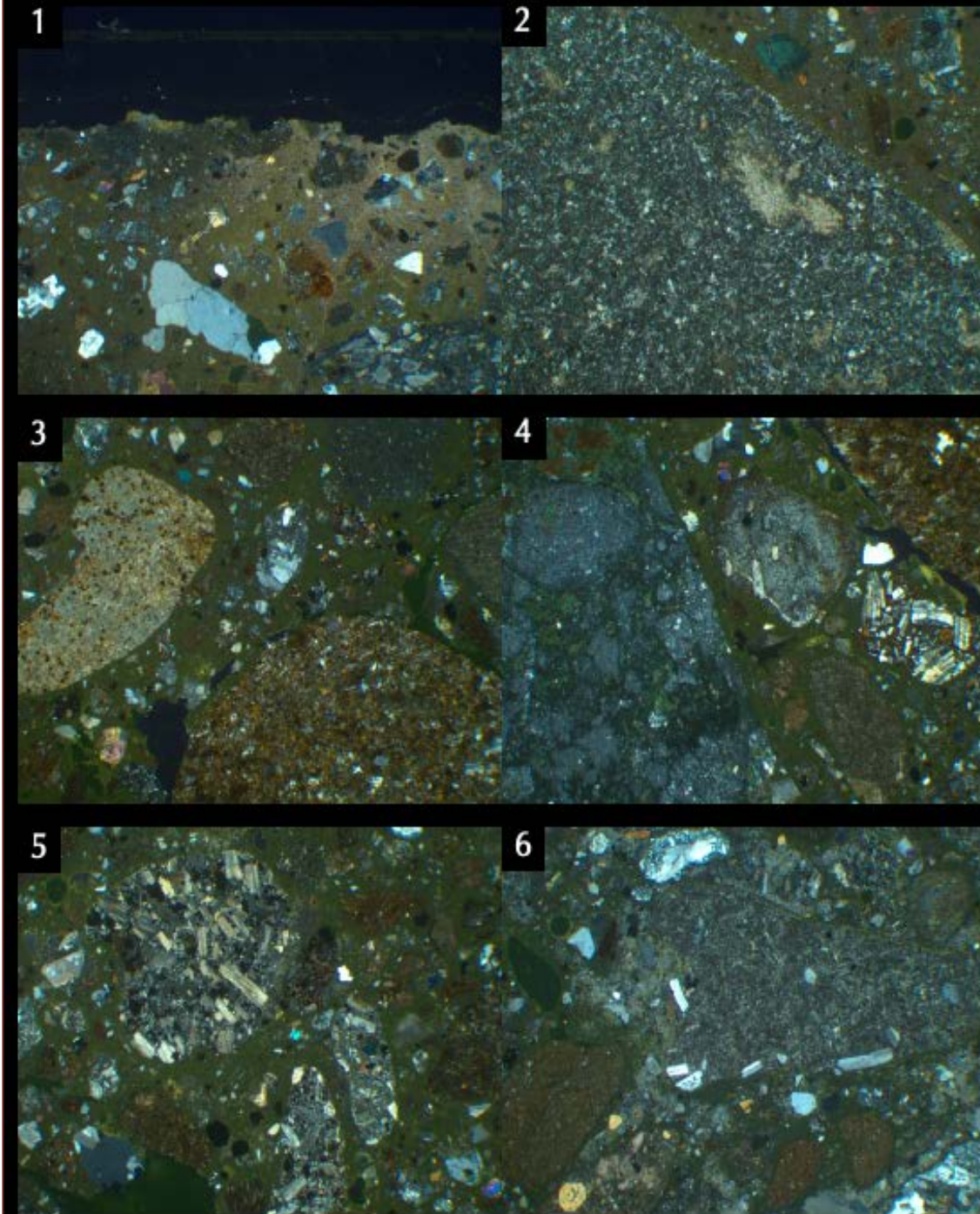


Figure 49: Micrographs of thin section of Core PR-C4 showing crushed gravel volcanic and volcaniclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

#	Microstructure
1	Carbonated exposed surface region of concrete and fragments of volcanic and volcaniclastic rocks, XPL
2	A dolomitic chert particle in coarse aggregate, XPL
3 to 6	Volcanic rocks in coarse aggregate and finer fragments in interstitial mortar fraction, XPL

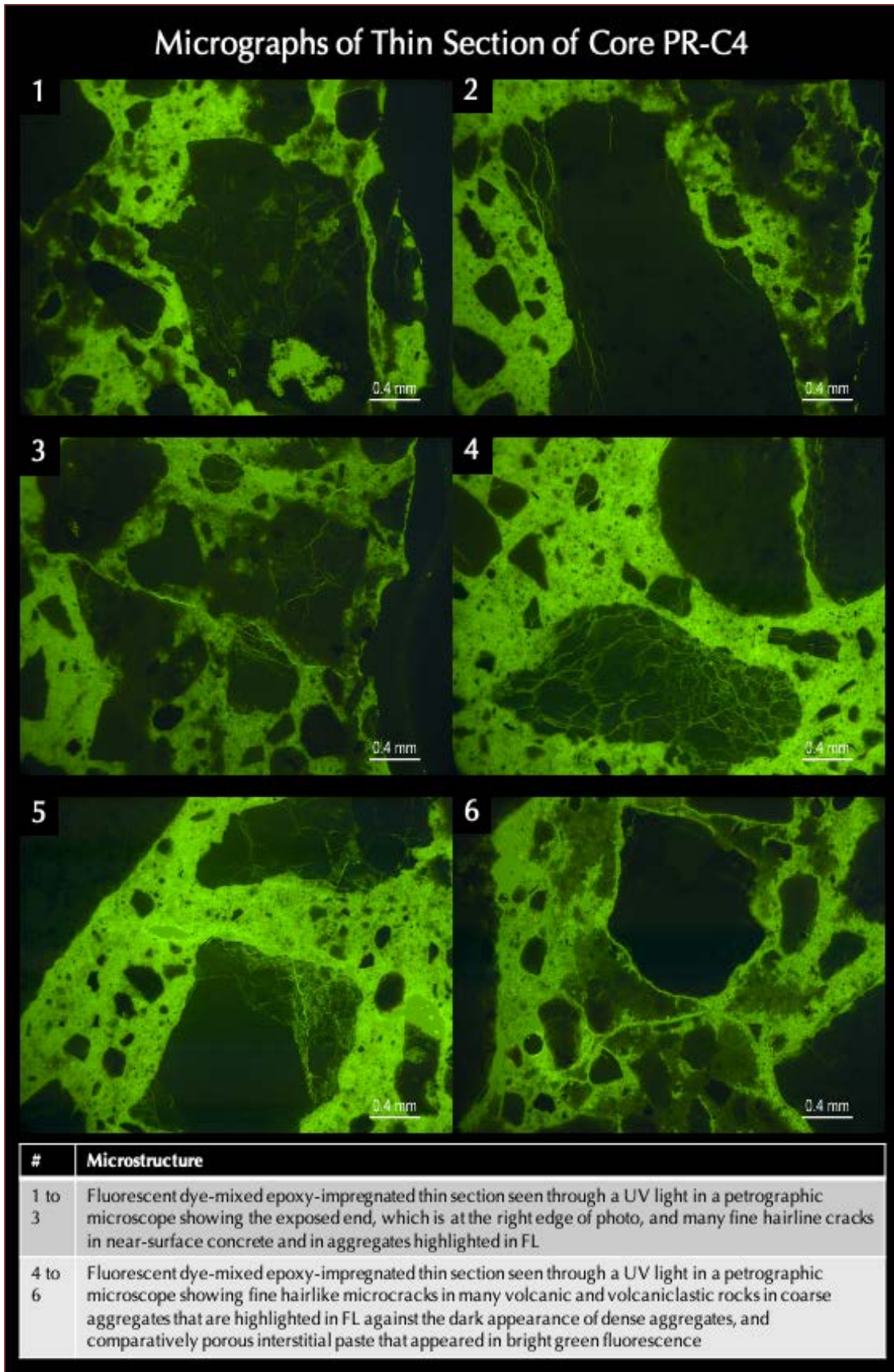


Figure 50: Micrographs of fluorescent dye-mixed epoxy-impregnated thin section of Core PR-C4 in UV light showing:

(a) The exposed weathered surface at right sides of top two photos,

(b) The main concrete body having relatively porous Portland cement paste that is highlighted in UV fluorescence whereas

(c) Dense aggregate particles that appeared dark in UV light except

(d) Some fine, hairline microcracks in aggregate particles that are highlighted in UV light (the purpose of this observation is to highlight those fine microcracks in aggregate particles).

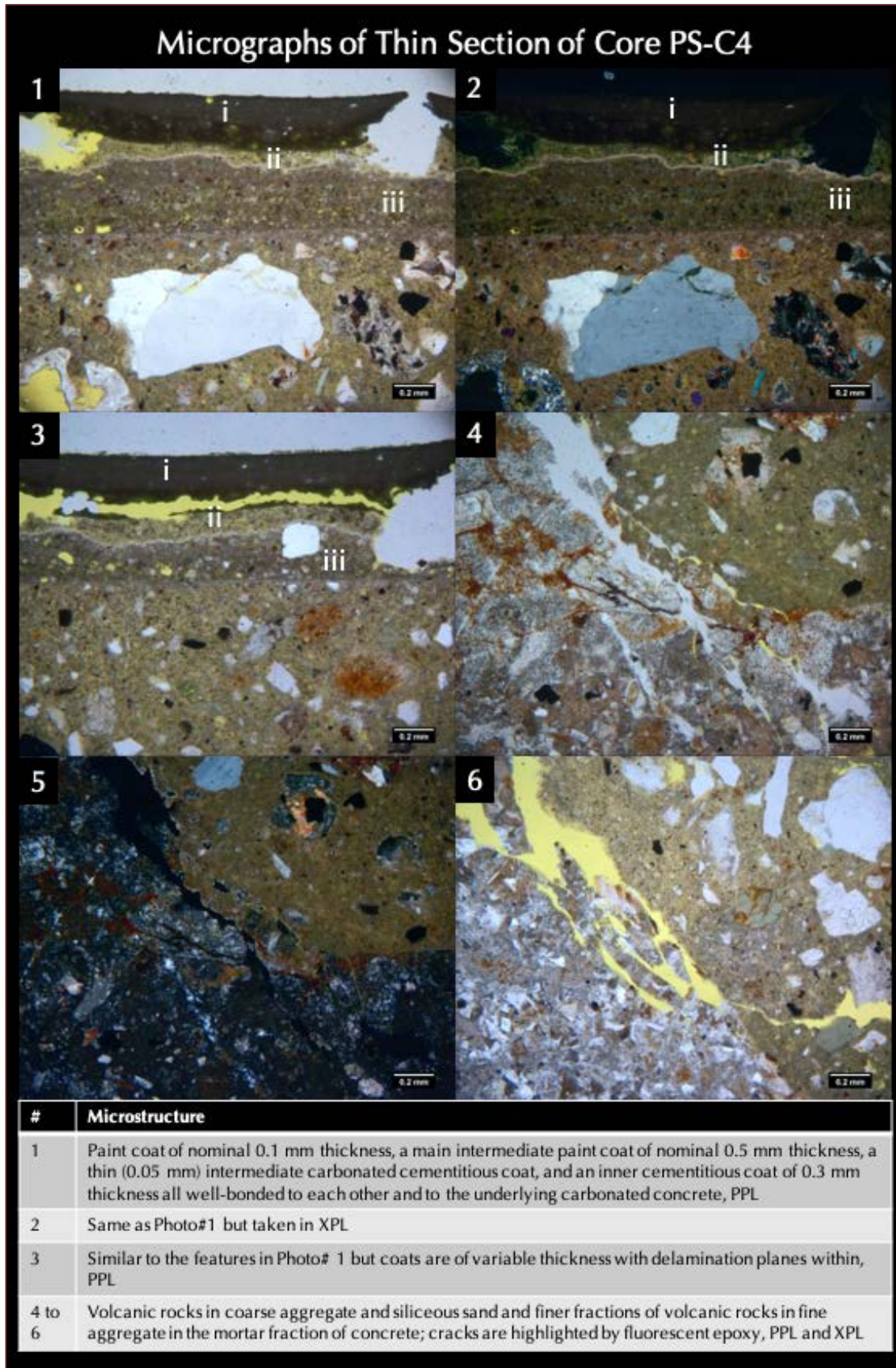


Figure 51: Micrographs of thin section of Core PS-C4 showing:

(a) The protective paint and cementitious coats applied in multiple layers marked as i, ii, and iii in the top row,

(b) The main concrete body containing crushed gravel volcanic and volcanoclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan, and,

(c) The carbonated surface region of concrete shown in the top row.

Micrographs of Thin Section of Core PS-C4

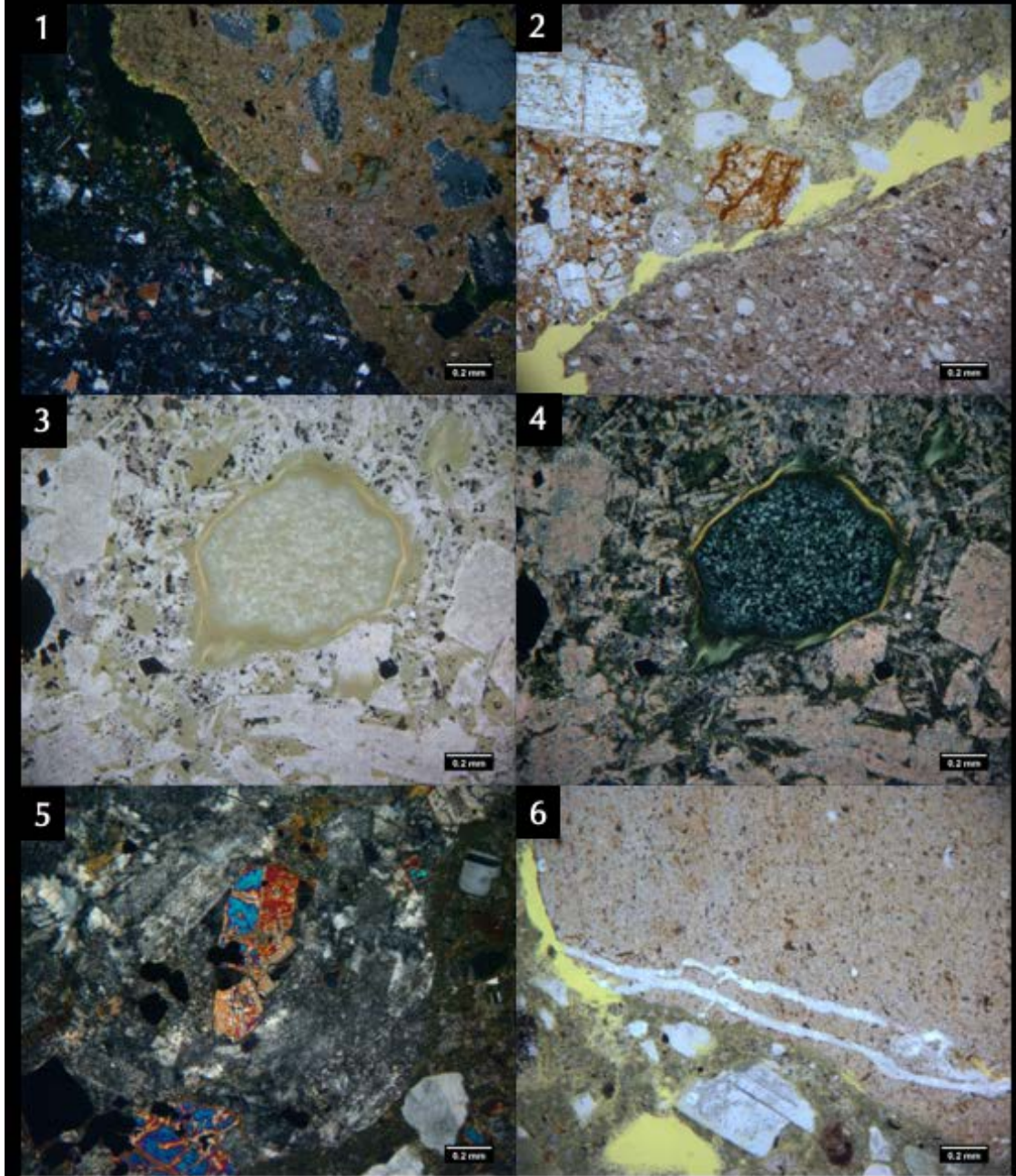


Figure 52: Micrographs of thin section of Core PS-C4 showing: crushed gravel volcanic and volcaniclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

#	Microstructure
1	Volcanic rocks in coarse aggregate and siliceous sand and finer fractions of volcanic rocks in fine aggregate in the mortar fraction of concrete; XPL
2	Volcanic rocks in coarse aggregate and siliceous sand and finer fractions of volcanic rocks in fine aggregate in the mortar fraction of concrete; cracks are highlighted by fluorescent epoxy, PPL
3	Palagonite glass in an altered volcanic rock, PPL
4	Same as Photo# 3 in XPL
5	Altered plagioclase and pyroxene phenocrysts in andesite coarse aggregate, XPL
6	Peripheral crack in a volcanic rock coarse aggregate

Micrographs of Thin Section of Core PS-C4

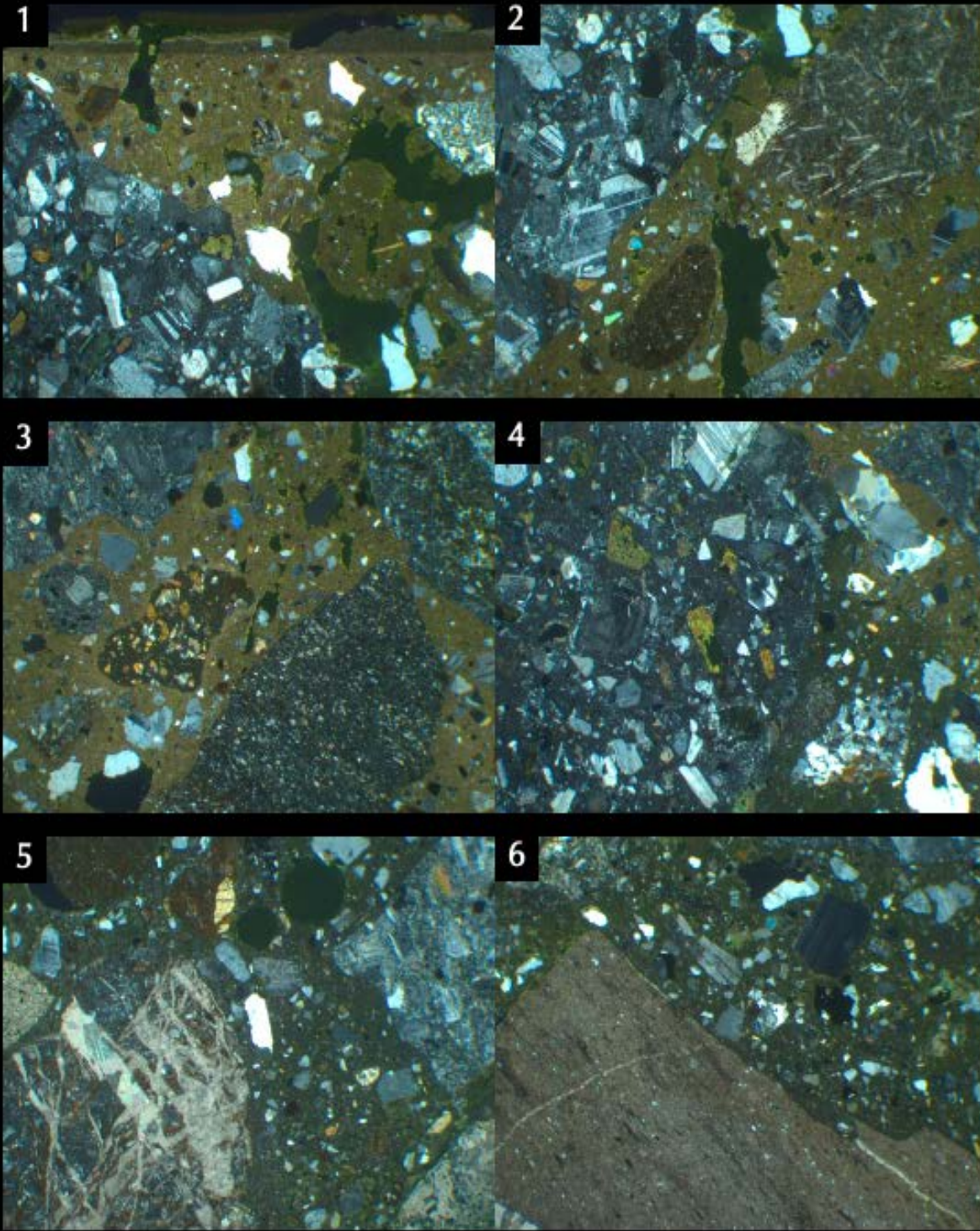


Figure 53: Micrographs of thin section of Core PS-C4 showing crushed gravel volcanic and volcanoclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

#	Microstructure
1 to 6	Volcanic rocks (andesite, rhyolite) in coarse aggregate and siliceous sand and finer fractions of volcanic rocks in fine aggregate in the mortar fraction of concrete; XPL

Micrographs of Thin Section of Core PS-C4

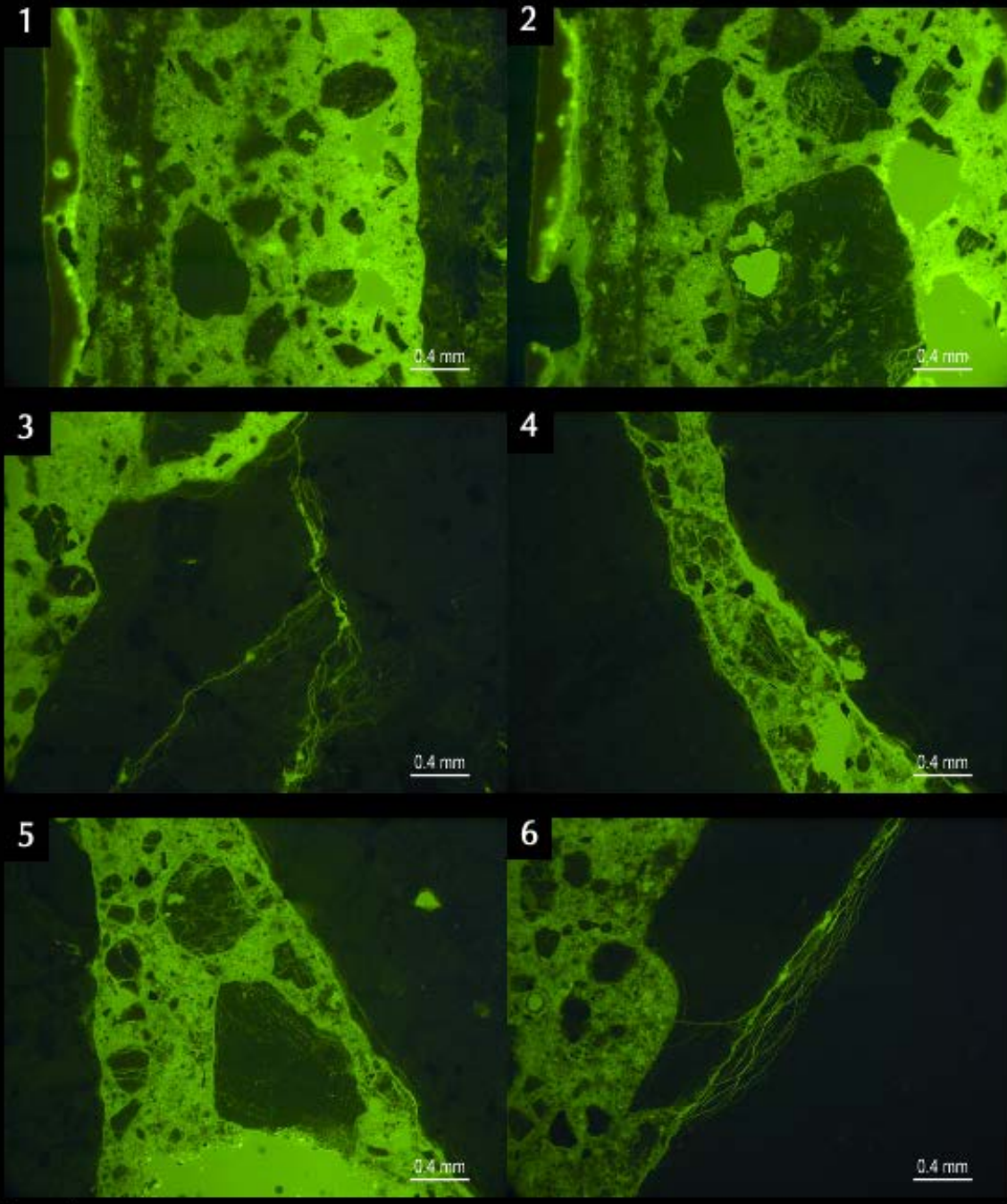


Figure 54: Micrographs of fluorescent dye-mixed epoxy-impregnated thin section of Core PS-C4 in UV light showing:

(a) The protective paint coats at the left sides of top two photos,

(b) The main concrete body having relatively porous Portland cement paste that is highlighted in UV fluorescence whereas

(c) Dense aggregate particles that appeared dark in UV light except

(d) Some fine, hairline microcracks in aggregate particles that are highlighted in UV light (the purpose of this observation is to highlight those fine microcracks in aggregate particles).

#	Microstructure
1, 2	Fluorescent dye-mixed epoxy-impregnated thin section seen through a UV light in a petrographic microscope showing the exposed end, which is at the left edge of photo, and many fine hairline cracks in near-surface concrete and in aggregates highlighted in FL.
3 to 6	Fluorescent dye-mixed epoxy-impregnated thin section seen through a UV light in a petrographic microscope showing fine hairlike microcracks in many volcanic and volcanoclastic rocks in coarse aggregates that are highlighted in FL against the dark appearance of dense aggregates, and comparatively porous interstitial paste that appeared in bright green fluorescence

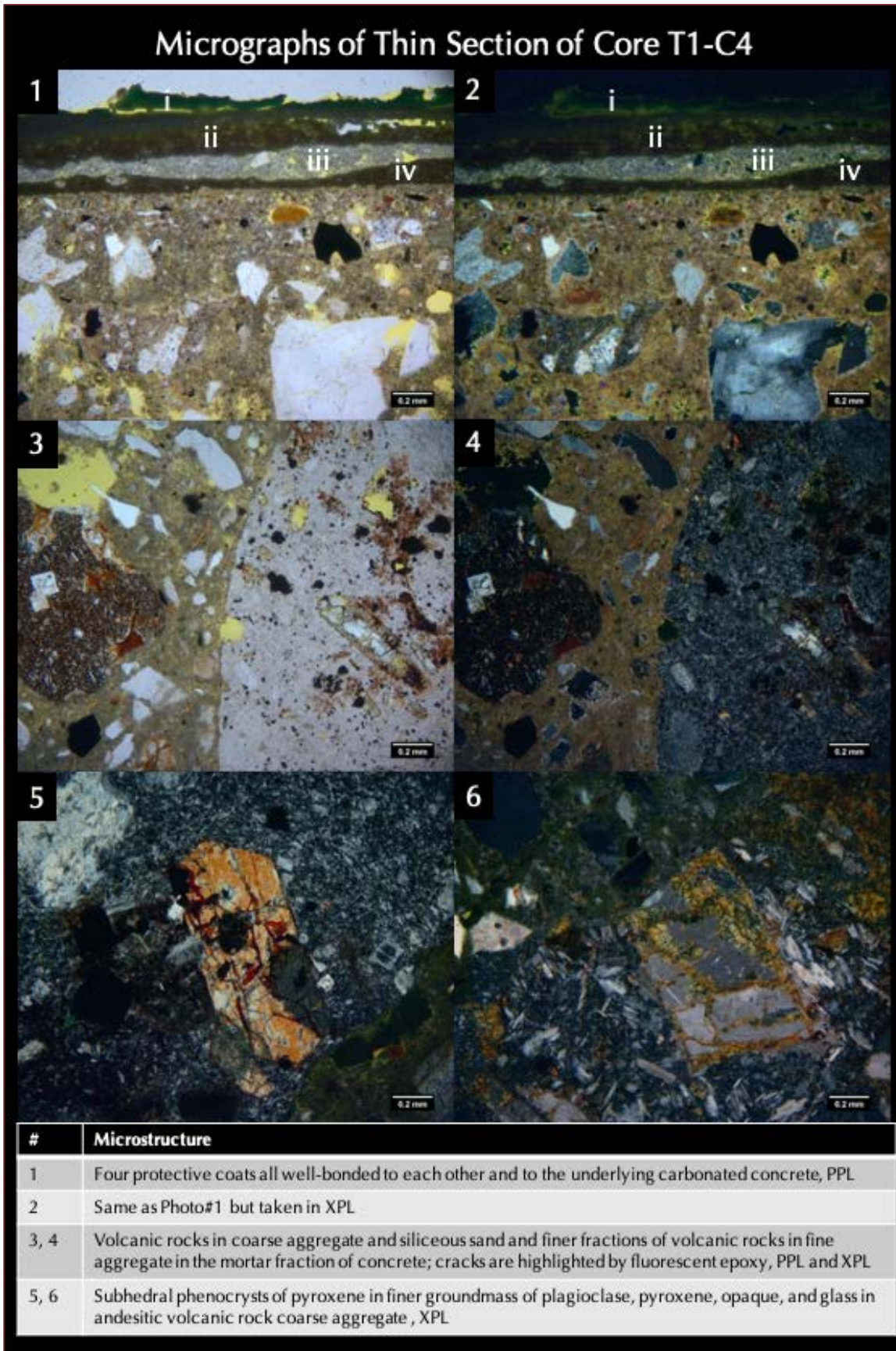


Figure 55: Micrographs of thin section of Core T1-C4 showing:

(a) The protective paint and cementitious coats applied in multiple layers marked as i to iv in the top row,

(b) The main concrete body containing crushed gravel volcanic and volcanoclastic coarse aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan, and,

(c) The carbonated surface region of concrete shown in the top row.

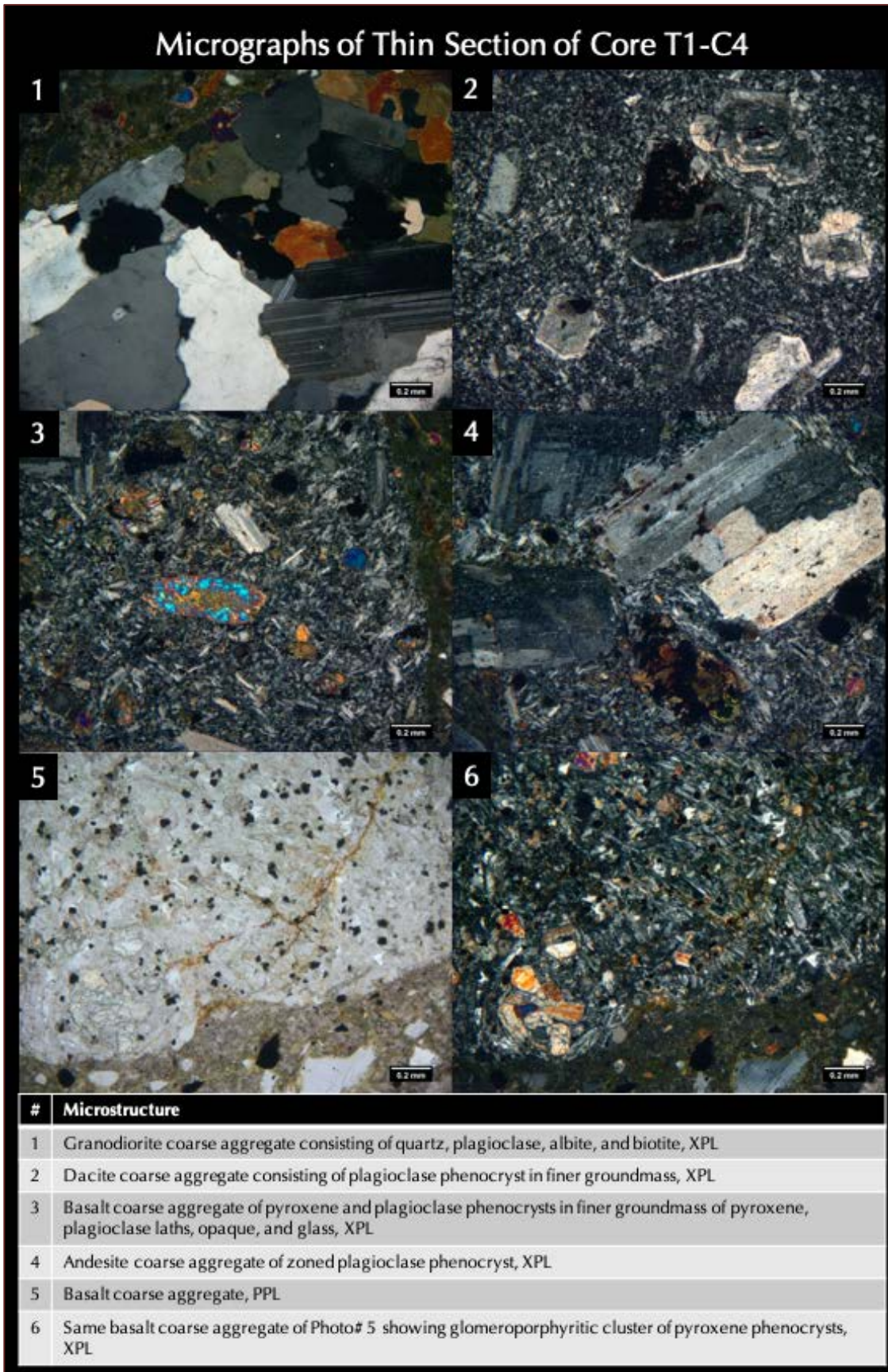


Figure 56: Micrographs of thin section of Core T1-C4 showing crushed gravel volcanic and volcanoclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

Micrographs of Thin Section of Core T1-C4

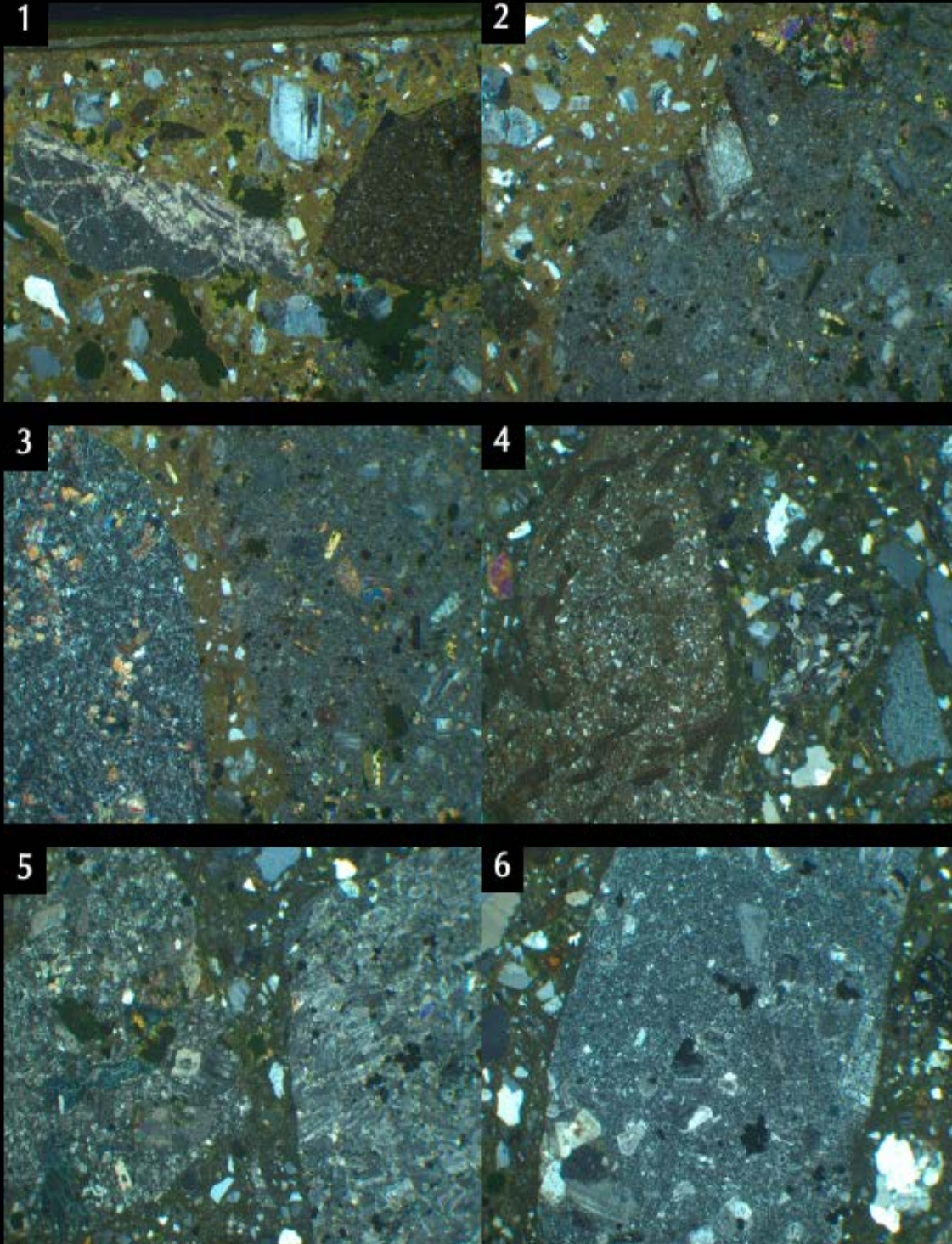


Figure 57: Micrographs of thin section of Core T1-C4 showing crushed gravel volcanic and volcanoclastic coarse aggregate and natural siliceous and finer volcanic rock and mineral fragments in fine aggregate particles, many of which show the typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan.

#	Microstructure
1 to 6	Volcanic rocks (andesite, rhyolite) in coarse aggregate and siliceous sand and finer fractions of volcanic rocks in fine aggregate in the mortar fraction of concrete; XPL

Micrographs of Thin Section of Core T1-C4

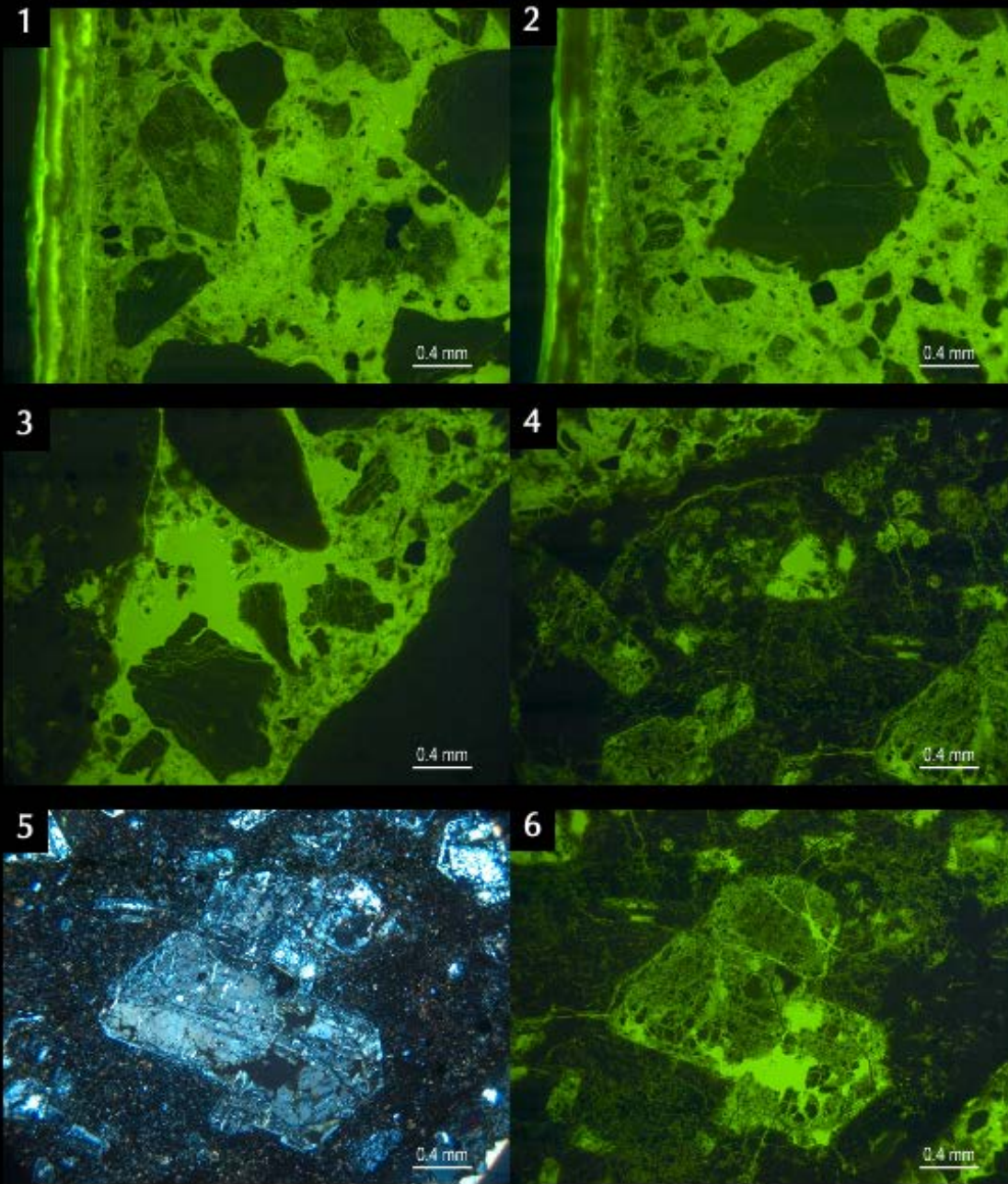


Figure 58: Micrographs of fluorescent dye mixed epoxy impregnated thin section of Core T1-C4 in UV light showing:

- (a) The protective paint coats at the left sides of top two photos,
- (b) The main concrete body having relatively porous Portland cement paste that is highlighted in UV fluorescence whereas
- (c) Dense aggregate particles that appeared dark in UV light except
- (d) Some fine, hairline microcracks in aggregate particles that are highlighted in UV light (the purpose of this observation is to highlight those fine microcracks in aggregate particles).

#	Microstructure
1, 2	Fluorescent dye-mixed epoxy-impregnated thin section seen through a UV light in a petrographic microscope showing the exposed end, which is at the left edge of photo, and many fine hairline cracks in near-surface concrete and in aggregates highlighted in FL
3, 4	Fluorescent dye-mixed epoxy-impregnated thin section seen through a UV light in a petrographic microscope showing fine hairlike microcracks in many volcanic and volcaniclastic rocks in coarse aggregates that are highlighted in FL against the dark appearance of dense aggregates, and comparatively porous interstitial paste that appeared in bright green fluorescence
5, 6	Altered subhedral plagioclase phenocryst in an andesite volcanic rock coarse aggregate shown in XPL and FL modes, respectively

PROTECTIVE COATINGS

Except for Core PR-C4 all other cores show the presence of a protective coating well-adhered to the underlying main concrete body. The coating appeared to have been applied in multiple layers, often having an interior cementitious coat on top of which paint coats were applied.

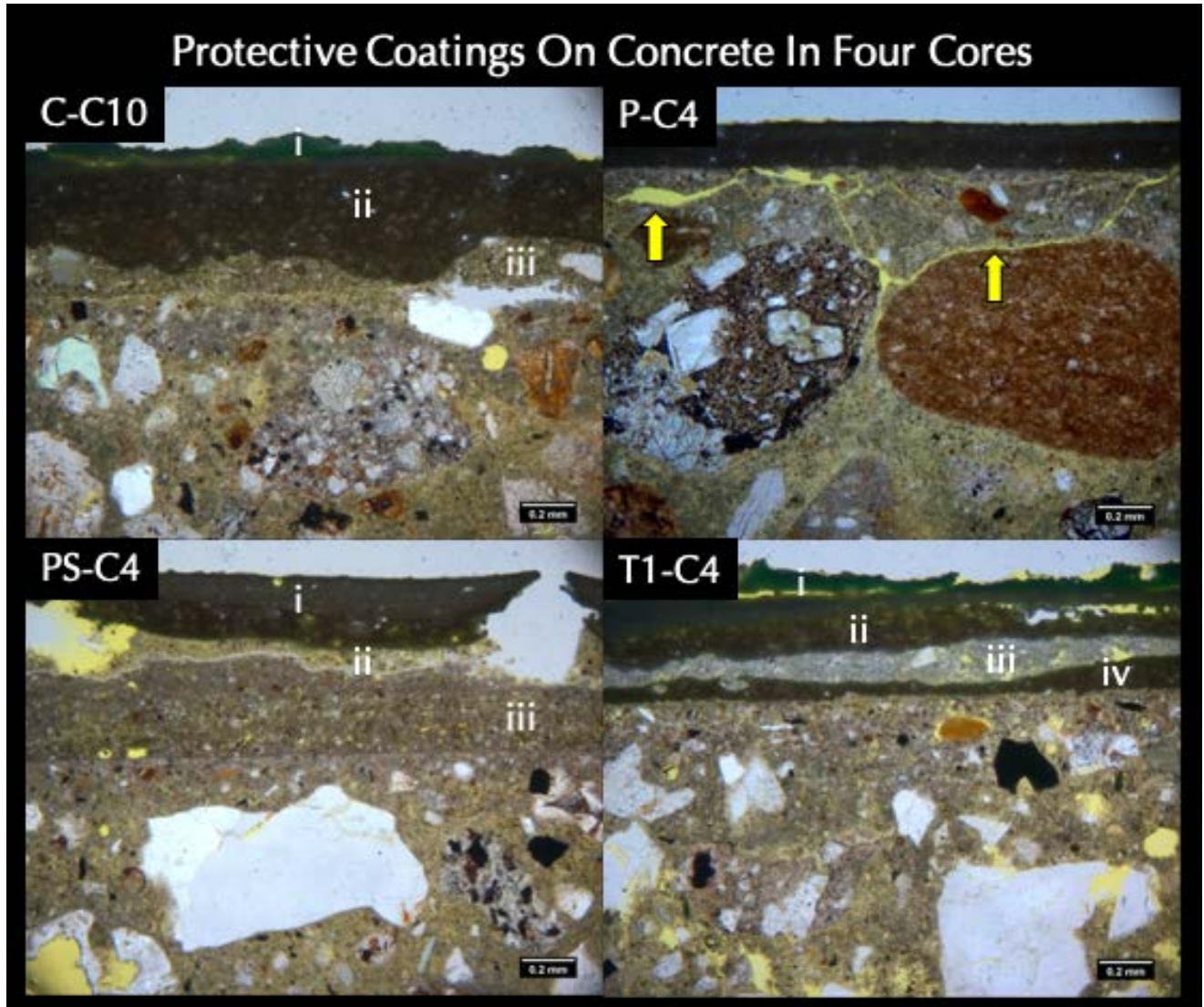


Figure 59: Protective Coatings on Concrete

For Core C-C10, three protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, a main intermediate paint coat of nominal 0.5 mm thickness, and an inner cementitious coat of 0.2 mm thickness all well-bonded to each other and to the underlying carbonated concrete.

For Core P-C4 one uniform paint coat is diagnosed having a nominal thickness of 0.2 mm, well-bonded to the underlying carbonated concrete. Immediately beneath the paint, the near-surface region of concrete showed some surface-parallel shrinkage microcracks.



For Core PS-C4, three protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, a main intermediate paint coat of nominal 0.5 mm thickness, and an inner cementitious coat of 0.3 mm thickness, all well-bonded to each other and to the underlying carbonated concrete. Immediately beneath the paint, as well as within the polymer paint and cementitious layers of coats, and the near-surface region of concrete showed some surface-parallel shrinkage microcracks.

For Core T1-C4, as many as four protective coats are diagnosed, consisting of (from exterior) a thin paint coat of nominal 0.1 mm thickness, two main intermediate paint coats each of variable but nominal 0.2 mm in thickness where the bottom coat contains calcite fillers in a different resin, followed by the innermost thinner (0.15 mm) coat all well-bonded to each other and to the underlying carbonated concrete.

COARSE AGGREGATES

Due to the plate tectonic setting of Puerto Rico at the boundary between two tectonic plates i.e., in an active subduction zone where North American plate is subducting against the Caribbean plate with the formation of many volcanic islands, the aggregates used in the concrete are derived from the local volcanic rocks under the andesite-dacite-rhyolite clan all having nominal maximum sizes of $\frac{3}{4}$ in. (19 mm). Particles are variably colored, dense and hard, subangular to subrounded, equidimensional to elongated, unaltered, uncoated, and mostly uncracked (except some altered volcaniclastic particles that showed internal microcracking). Particles are well-distributed throughout the lengths of the cores and well-graded.

Despite potential alkali-silica reactivity of many of these volcanic rocks, e.g., from andesite to dacite and rhyolite where the glassy component in the groundmass of volcanic rocks are potentially reactive components to participate in deleterious alkali-silica reactions with the cement alkalis and high moisture, there is no evidence of such a reaction of volcanic rocks found in the cores. Coarse aggregate particles are present in sound conditions without any physical or chemical deterioration.

FINE AGGREGATES

Fine aggregates are compositionally similar mixtures of fine-grained volcanic rocks (basalt-andesite-trachyte-rhyolite) of coarse aggregates, natural siliceous sands of quartz, quartzite, feldspar, chert, etc., and a minor amount of seashells in both cores having nominal maximum sizes of $\frac{3}{8}$ in. (9.5 mm). Particles are subangular to subrounded, dense, hard, variably colored from colorless to light gray to brown to pink, well-graded and well-distributed. There is no evidence of alkali-aggregate reaction of fine aggregate particles. Fine aggregate particles have been sound during their service.



The following Table summarizes properties of coarse and fine aggregates determined from the cores:

Properties and Compositions of Aggregates	All Five Cores
Coarse Aggregates	
Types	Volcanic rocks - crushed gravel of andesite-dacite-rhyolite clan
Nominal maximum size (in.)	³ / ₄ in. (19 mm)
Rock Types	Andesite-trachyte clan
Angularity, Density, Hardness, Color, Texture, Sphericity	Variably colored, dense and hard, subangular to subrounded, equidimensional to elongated,
Cracking, Alteration, Coating	Unaltered, uncoated, and mostly uncracked (except some altered volcanoclastic particles that showed internal microcracking)
Grading & Distribution	Particles are well-graded and well-distributed
Soundness	Sound
Alkali-Aggregate Reactivity	None
Fine Aggregates	
Types	Compositionally similar mixtures of fine-grained volcanic rocks (basalt-andesite-trachyte-rhyolite) of coarse aggregates, natural siliceous sands of quartz, quartzite, feldspar, chert, etc., and a minor amount of seashells
Nominal maximum size	³ / ₈ in. (9.5 mm)
Rock Types	Fine-grained volcanic rocks (basalt-andesite-trachyte-rhyolite) of coarse aggregates, natural siliceous sands of quartz, quartzite, feldspar, chert, etc., and a minor amount of seashells
Cracking, Alteration, Coating	Particles are variably colored (colorless, light gray, brown, pink), subangular to subrounded, dense, hard, equidimensional to elongated
Grading & Distribution	Well-graded and Well-distributed
Soundness	Sound
Alkali-Aggregate Reactivity	None

Table 2: Properties of coarse and fine aggregates of concretes.

PASTE

Concretes in all five cores contain Portland cement pastes, which are moderately gray to beige, hard, and dense. Freshly fractured surfaces have subvitreous lusters and subconchoidal textures. Residual and relict Portland cement particles are present in the sound interior bodies and estimated to constitute 6 to 8 percent of the paste volumes. The calcium hydroxide component of cement hydration occurs as small, platy, patchy units in the sound interior bodies and is estimated to constitute 8 to 10 percent of the paste volume. Hydration of Portland cement is normal. The textural and compositional features of the pastes are indicative of Portland cement contents similar in both cores and estimated to be approximately 5¹/₂ to 6 bags per cubic yard; and water-cement ratios uniform throughout the bodies of the cores and estimated to be 0.40 to 0.45. There is no evidence of deleterious secondary deposits in any core.



Carbonation of pastes extended to nominal depths of 10 to 15 mm at the exposed surface ends beneath the protective coats. Bonds between the coarse and fine aggregate particles and pastes are tight. There is no evidence of any deleterious micro or macro-cracking of concrete in the sound interior bodies of the cores except some fine hairline shrinkage microcracks found at the top 10 to 15 mm of the exposed surface regions, which are judged to have formed due to drying of concrete prior to the application of protective coats.

Properties and Compositions of Paste	All Five Cores
Color, Hardness, Porosity, Luster	Gray to Beige, hard, and dense, freshly fractured surfaces have subvitreous lusters and subconchoidal textures
Residual Portland Cement Particles	Normal, 6 to 8 percent by paste volume in the sound interior concretes
Calcium hydroxide from cement hydration	Normal, 8 to 10 percent by paste volume in the sound interior concretes
Pozzolans, Slag, etc.	None
Water-cementitious materials ratio (w/cm), estimated	0.40 to 0.45, uniform throughout the sound interior bodies of cores
Cementitious materials contents, estimated (equivalent to bags of Portland cement per cubic yard)	5 ^{1/2} to 6
Secondary Deposits	None
Depth of Carbonation, mm	Carbonation of pastes extended to nominal depths of 10 to 15 mm at the exposed surface ends beneath the protective coats
Microcracking	There is no evidence of any deleterious micro or macro-cracking of concrete in the sound interior bodies of the cores except some fine hairline shrinkage microcracks found at the top 10 to 15 mm of the exposed surface regions
Aggregate-paste Bond	Tight in the sound interior concretes
Bleeding, Tempering	None
Chemical deterioration	None in the interior concretes

Table 3: Properties and composition of hardened cement pastes.

There is no evidence of deleterious secondary deposits in the cores. Bonds between the coarse and fine aggregate particles and pastes are tight. There is no evidence of any deleterious micro or macro-cracking of concrete in the sound interior bodies of the cores. The top 15 mm of exposed surface regions show shrinkage microcracks which were formed due to drying of concrete prior to the placement of protective coats.

AIR

Air occurs as coarse, near-spherical and irregularly shaped voids having sizes up to 4 mm, which are characteristic of entrapped air. Concretes in all five cores are non-air-entrained, having estimated air contents of less than 1 to 3 percent.



WATER-SOLUBLE CHLORIDE AND SULFATE CONTENTS

Table 4 and Figures 60 to 64 show results of water-soluble chloride and sulfate contents of concrete determined from ion chromatography (a la ASTM D 4327) on pulverized sections from the top exposed ends, mid-depth locations, and the bottom ends of cores.

Core ID & Depth of Sample Section		Water-Soluble Chloride & Sulfate Contents from Ion Chromatography		
		% Chloride by mass of concrete	% Chloride by mass of cement (assuming 15% cement in normal-weight concrete)	Water-soluble Sulfate
C-C10 Channel	0-15 mm	0.004	0.026	0.169
	85-95 mm	0.002	0.013	0.108
	150-170 mm	0.002	0.013	0.129
P-C4 PIT	0-15 mm	0.003	0.020	0.210
	65-80 mm	0.003	0.020	0.216
	155-170 mm	0.003	0.020	0.189
PS-C4 Pump Station	0-15 mm	0.005	0.033	0.186
	60-75 mm	0.003	0.020	0.120
	110-120 mm	0.002	0.013	0.118
PR-C4 Recirculation Pump	0-15 mm	0.031	0.20	0.255
	65-85 mm	0.005	0.033	0.232
	130-150 mm	0.005	0.033	0.192
T1-C4 Anaerobic Tank 1	0-15 mm	0.006	0.040	0.189
	55-70 mm	0.006	0.040	0.183
	115-135 mm	0.004	0.026	0.149

Table 4: Water-soluble chloride and sulfate contents from the exposed, mid-depth, and bottom ends of cores. Values are all lower than common industry-recommended maximum threshold limit of 0.2 percent chloride by mass of cement to cause corrosion of steel in concrete in the presence of oxygen and moisture.

Despite the reported location of the plant in a marine environment and the nature of its past usage, all five cores show negligible chloride contents at the exposed ends and in the interiors to remove the possibility of chloride-induced corrosion of reinforcing steel in the concrete. Any steel corrosion would then be carbonation-induced, which probably would have occurred prior to the placement of protective coats. Sulfate contents are indicative of sulfates from Portland cement with no introduction of an excess sulfate from the marine environment or wastewater containments in the plant.

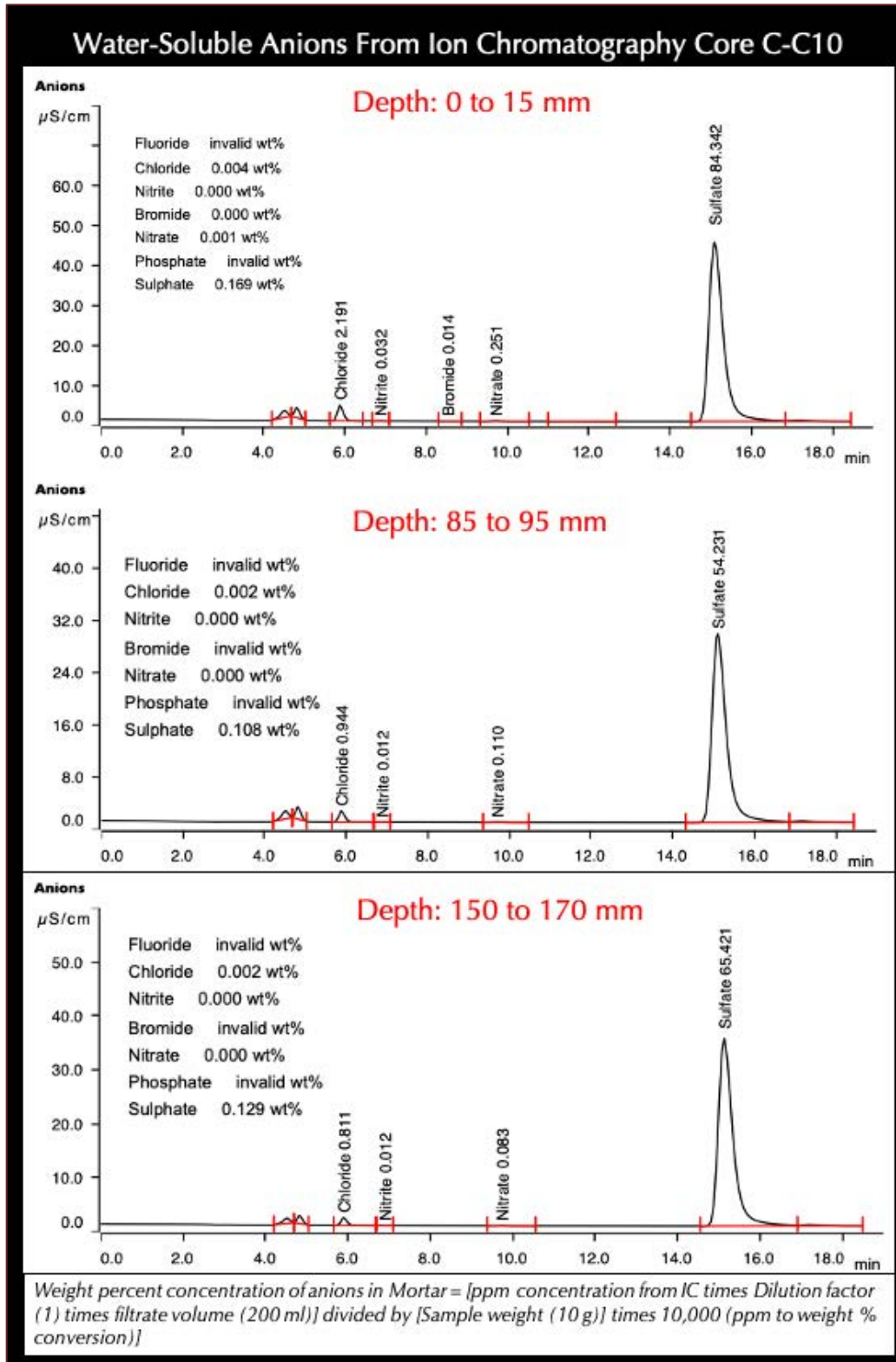


Figure 60: Ion chromatographs of water-soluble anions from the top, mid-depth, and bottom ends of Core C-C10.

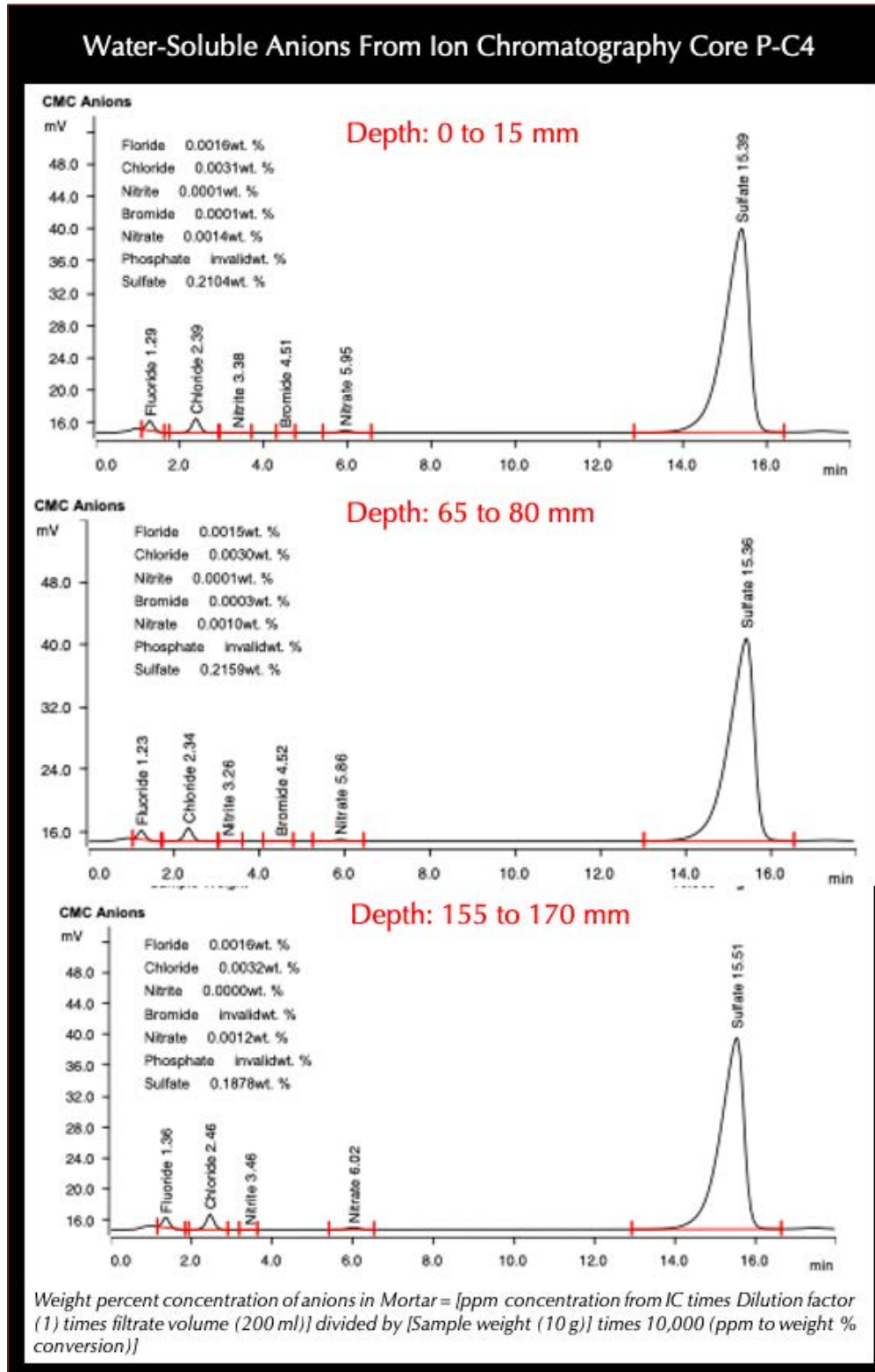


Figure 61: Ion chromatographs of water-soluble anions from the top, mid-depth, and bottom ends of Core P-C4.

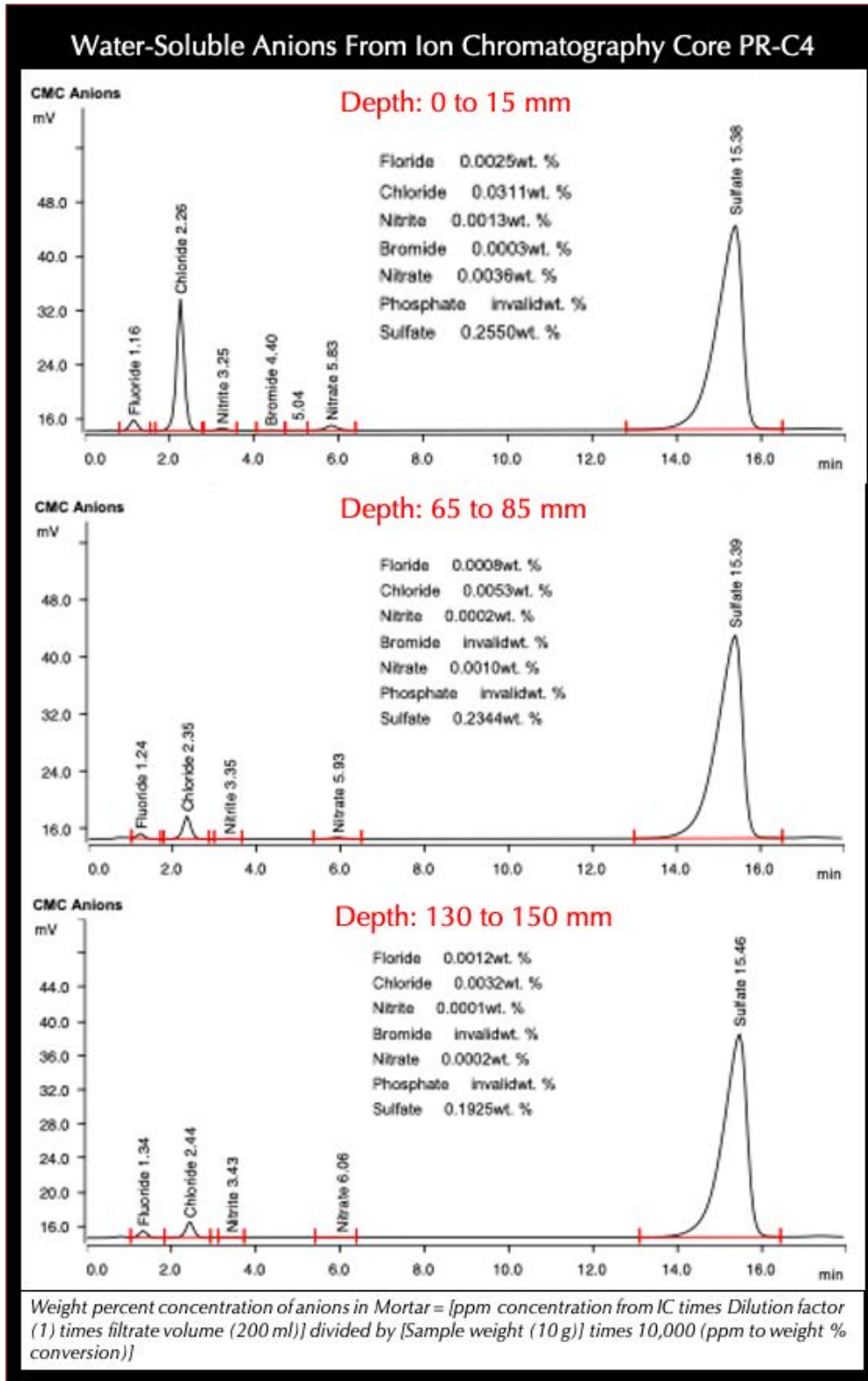


Figure 62: Ion chromatographs of water-soluble anions from the top, mid-depth, and bottom ends of Core PR-C4.

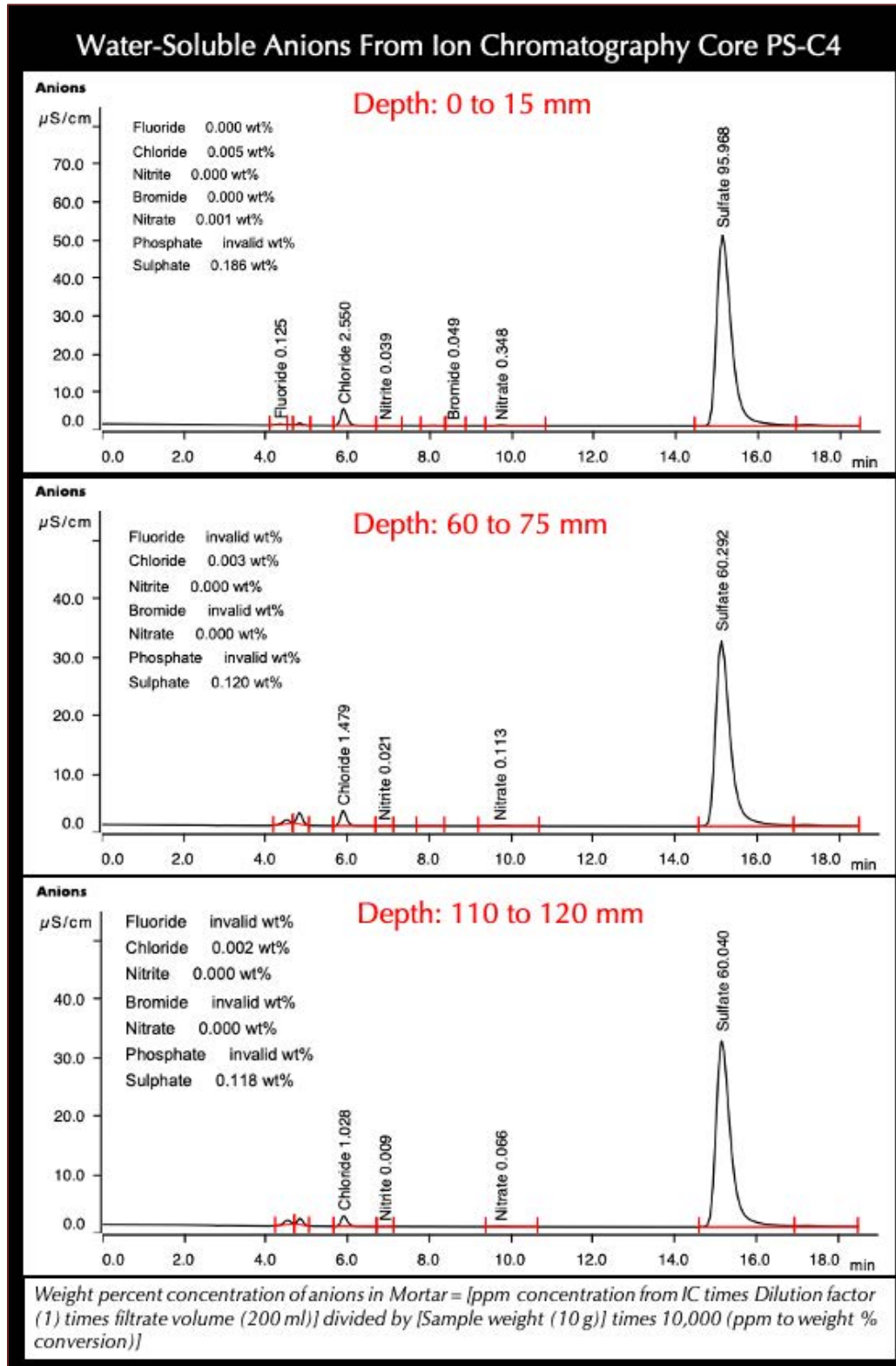


Figure 63: Ion chromatographs of water-soluble anions from the top, mid-depth, and bottom ends of Core PS-C4.

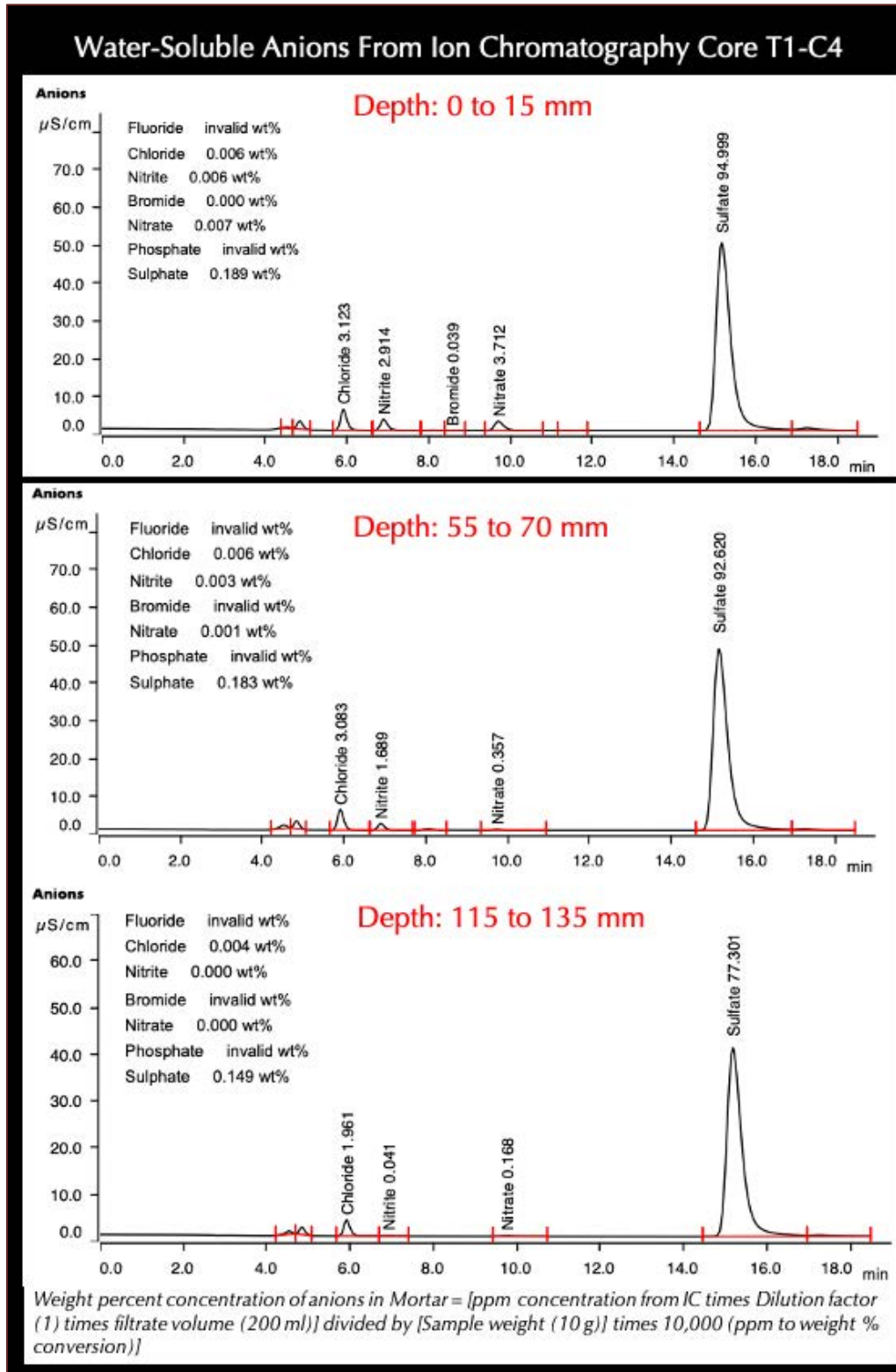


Figure 64: Ion chromatographs of water-soluble anions from the top, mid-depth, and bottom ends of Core T1-C4.

FTIR SPECTROSCOPY OF PAINT COATS

Figures 65 to 67 show FTIR spectra of paint coats applied on the exterior concrete surfaces in Cores C-C10, PS-C4, and T1-C4, respectively.

Paint applied in all three cores are found to be compositionally similar, which is determined to be of polyvinyl acetate composition. Also detected with paint is a separate cementitious coat in Cores C-C10 and PS-C4, which are shown in Figure 59.

Absorbance bands other than the resins are found to contain calcite, talc, and clay fillers which are common fillers in paint.

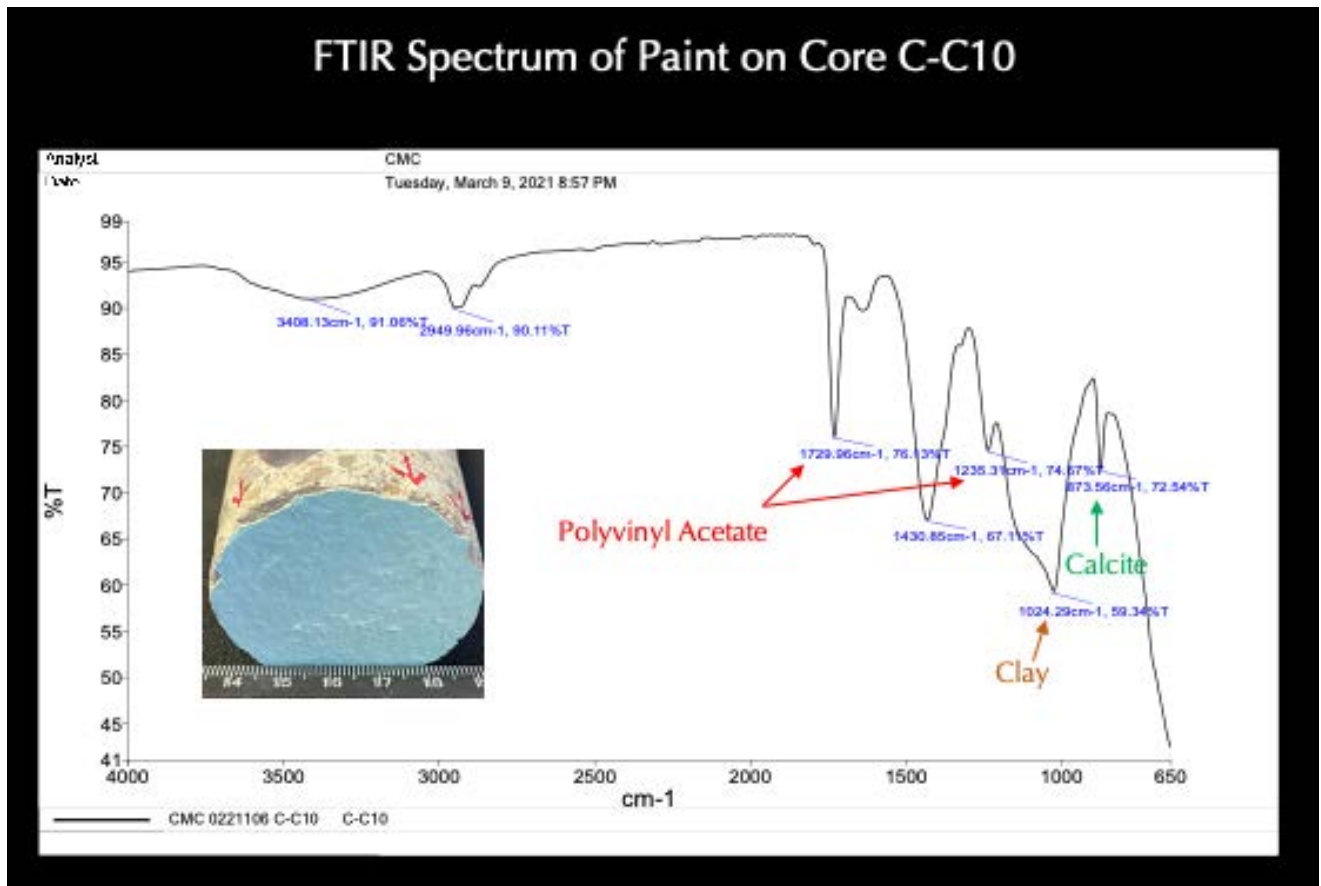


Figure 65: FTIR spectra of paint coats on Core C-C10.

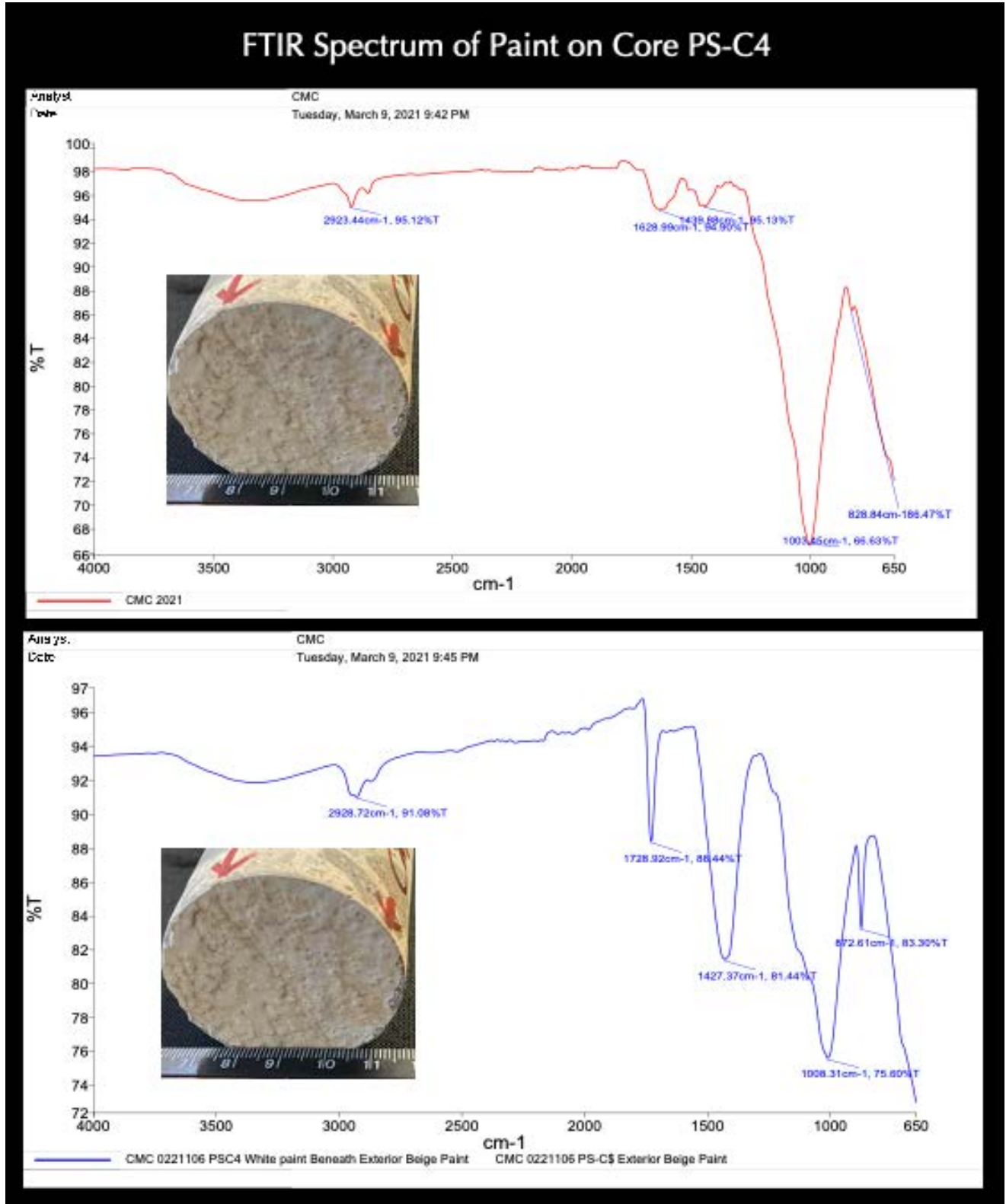


Figure 66: FTIR spectra of paint coats on Core PS-C4.

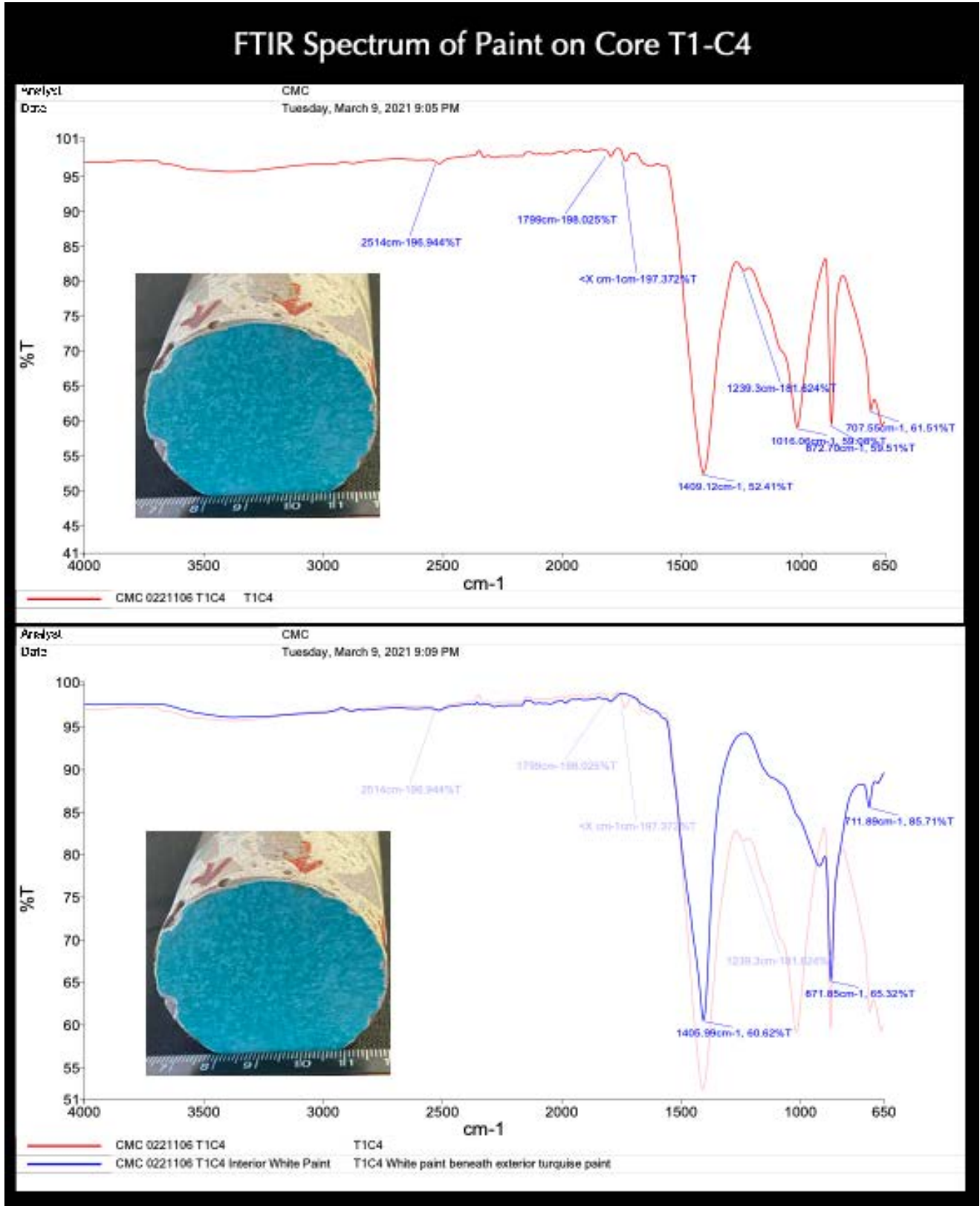


Figure 67: FTIR spectra of paint coats on Core T1-C4.



DISCUSSIONS

The concrete in all five cores from five different structural elements of the WWTP are found to be compositionally similar and indicative of use of the same concrete mix. The concrete contains: (i) crushed volcanic and volcanoclastic gravel coarse aggregates having nominal maximum sizes of 3/4 in. which are well-graded, well-distributed, subangular to subrounded, sound, and show many typical volcanic textures and mineralogies of basalt-andesite-trachyte-dacite clan, (ii) natural siliceous sand fine aggregate with some calcareous seashells and finer fractions of volcanic rock fragments, (iii) Portland cement pastes, having cement contents estimated to be 5 1/2 to 6 bags per cubic yard, without any other pozzolanic or cementitious materials, and water-cement ratios uniform throughout the depth of each core and estimated to be 0.40 to 0.45, and (iv) many interstitial voids except any intentionally introduced entrained air for the concretes to be non-air-entrained (estimated 1 to 3 percent total air).

The overall condition of the interior concretes in all five cores are found to be sound and serviceable mainly due to the performance of protective coatings to prevent any migration of elements from the environments. Based on deep carbonation in cores to depths of 15 mm as well as some near-surface microcracking at the top 15 mm of exposed surfaces, carbonation-induced corrosion of steel may have occurred to cause cracking and spalling from rebar corrosion, but none of the cores show any elevated chloride to cause any chloride-induced corrosion. The overall qualities and conditions of concretes in the main bodies of cores are judged to be sound with no evidence of any physical or chemical deterioration. The interior concretes are dense, well-consolidated, and should be serviceable in their intended environment as long as they are well-protected by the protective coatings to prevent penetration of moisture, chloride, and other corrosive agents to cause further corrosion of steel, and corrosion-related spalling.

REFERENCES

ASTM C 856 "Standard Practice for Petrographic Examination of Hardened Concrete," Vol. 4.02, ASTM International, West Conshohocken, PA, 2016.

Jana, D., "Sample Preparation Techniques in Petrographic Examinations of Construction Materials: A State-of-the-art Review," *Proceedings of the 28th Conference on Cement Microscopy*, International Cement Microcopy Association, Denver, Colorado, pp. 23-70, 2006.

ASTM C 1218, "Standard Test Method for Water-Soluble Chloride in Mortar and Concrete," Vol. 4.02, ASTM International, West Conshohocken, PA, 2010.

ASTM D 4327, "Standard Test Method for Anions in Water by Suppressed Ion Chromatography," Vol. 11.01, ASTM International, West Conshohocken, PA, 2019.

★ ★ ★ END OF TEXT ★ ★ ★

The above conclusions are based solely on the information and samples provided at the time of this investigation. The conclusion may expand or modify upon receipt of further information, field evidence, or samples. Samples will be disposed after submission of the report as requested. All reports are the confidential property of clients, and information contained herein may not be published or reproduced pending our written approval. Neither CMC nor its employees assume any obligation or liability for damages, including, but not limited to, consequential damages arising out of, or, in conjunction with the use, or inability to use this resulting information.



END OF REPORT¹

¹ The CMC logo is made using a lapped polished section of a 1930's concrete from an underground tunnel in the U.S. Capitol.