

## ESEM-EDS Investigation of the Weathering of a Heritage Sydney Sandstone

Kin Hong Ip, Barbara Stuart,\* Abhi Ray, and Paul Thomas

Department of Chemistry and Forensic Sciences, University of Technology Sydney, P.O. Box 123, Broadway NSW 2007, Australia

**Abstract:** The degradation of Sydney sandstone used to build the heritage St Mary's Cathedral in Sydney, Australia, has been investigated using environmental scanning electron microscopy combined with energy dispersive X-ray spectroscopy. This technique provided the structural details of the cementing clay and an elemental characterization of the sandstone. The observed differences in the elemental composition of the unweathered and weathered sandstones were associated with changes to the clay microstructure upon weathering. The results support the substitution theory that  $\text{Fe}^{3+}$  replaces  $\text{Al}^{3+}$  in the kaolinite clay component upon weathering. An examination of the impurities present prior to a nonstructural iron removal treatment revealed the presence of minerals that may provide a source of the elements responsible for the substitution process.

**Key words:** sandstone, clay, kaolinite, weathering, environmental scanning electron microscopy, energy dispersive X-ray spectroscopy

### INTRODUCTION

Various 19th century heritage buildings located in Sydney, Australia, are built from locally quarried "yellow block" sandstone. Sydney yellow block sandstones typically contain 60–68% sand bound together with a clay-based matrix (16–25%) and small quantities of iron-rich impurities (McNally & Franklin, 2000). Oxidation of the iron-rich minerals in the stone produces an attractive golden color. As a result of exposure to environmental factors, a number of Sydney heritage buildings are showing evidence of deterioration. Although the sandstone does retain detailed carving and the integrity of the stone structure, the material becomes relatively brittle and susceptible to damage.

St Mary's Cathedral is a significant public building in central Sydney and was built in the mid-19th century of sandstone quarried in the Pyrmont area of the city (Fig. 1). Decayed sandstone from the Cathedral has been replaced by new Pyrmont sandstone as part of a restoration program by the Government Architect's Office of the New South Wales Department of Commerce in collaboration with Gosford Quarries Pty Ltd. To best manage the conservation of heritage sandstone buildings, including St Mary's Cathedral, there is a need to fully understand the nature of the degradation process observed.

In this study, the clay component of sandstone removed from St Mary's Cathedral has been examined using environmental scanning electron microscopy (ESEM) combined with elemental analysis via energy dispersive X-ray spectroscopy (EDS). This study forms part of a series of investigations dealing with the different aspects of the weathering process of Sydney sandstones (Friolo et al., 2003, 2004, 2005a, 2005b; Ip et al., 2008a, 2008b). The earlier

studies have involved the use of spectroscopic techniques and X-ray diffraction to examine the structural changes to weathered clay, and thermal analysis has revealed changes to the transitions associated with the clay. Such studies have been used to postulate a substitution model responsible for the observed physical changes observed upon weathering. However, as this model involves changes to the elemental composition of the clay, it was believed important to characterize the changes to the elements present in the clay structure and EDS provides a suitable tool.

### MATERIALS AND METHODS

Sandstone samples from St Mary's Cathedral were supplied by Gosford Quarries Pty Ltd, Australia. The samples obtained were the more decayed yellow block sandstones that had been removed and replaced. The weathered surfaces were separated from the unweathered cores of the decayed stones by use of a diamond saw, and small amounts of water were employed as a coolant during cutting. Examples of freshly exposed unweathered Sydney sandstone and weathered stone are illustrated in Figure 2.

The clay-based material was separated from the sandstone samples for SEM analysis. Both weathered and unweathered sandstones were manually crushed using a mortar and pestle and then mixed with distilled water ( $5 \text{ gL}^{-1}$ ). An ultrasonic probe with frequency of 20 kHz and energy of 20 W was used to dislodge the clay-based material from the sand particles (Schmidt et al., 1999; Roscoe et al., 2000). The decanted clay materials were suspended in distilled water and particles  $\leq 2 \mu\text{m}$  were collected using a gravity settling method according to Stokes' Law (Rutledge et al., 1967; Carroll, 1970). The clay collected by centrifugation was dried in a  $50^\circ\text{C}$  oven overnight and separated into two portions. One portion was stored in a desiccator until

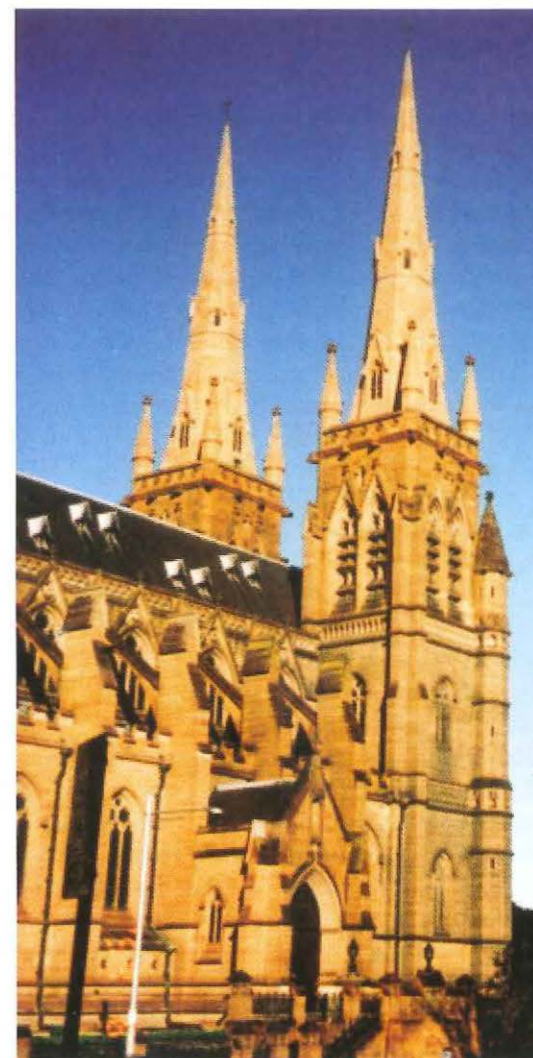


Figure 1. St Mary's Cathedral, Sydney.

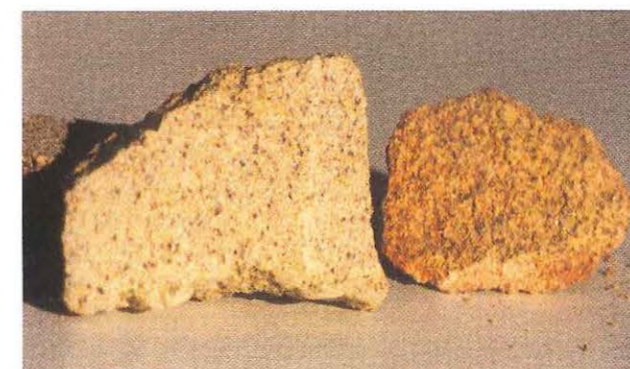


Figure 2. Unweathered (left) and weathered (right) Sydney sandstone.

analysis, and the second portion was further treated with  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaHCO}_3$  to remove nonstructural iron from the clay samples (Mehra & Jackson, 1960).

A Philips XL30 ESEM, on which an energy dispersive X-ray spectrometer was mounted, was used for the analysis of the clay samples before and after the removal of nonstruc-

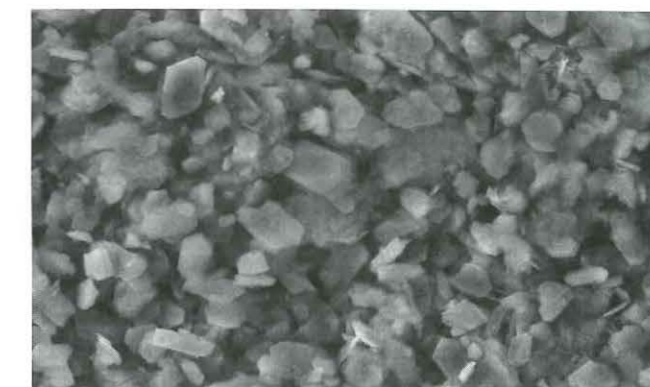


Figure 3. Electron micrograph of unweathered clay after nonstructural iron removal ( $156 \mu\text{m}$  width of field).

tural iron from each sample. Separated clay samples were secured onto the sample holder using double-sided tape. An accelerating voltage of 15.0 kV was used in the microscopic analysis, and a backscattering detector was used to collect electronic images. Images were produced along the sides and the centers of each sample, and different magnifications from the same point of the samples were also recorded.

### RESULTS

The electron micrographs of both the weathered and unweathered cementing clays after nonstructural iron removal show that a large number of hexagonal platelets of various sizes are present. There is no dramatic difference in the appearance of the weathered and unweathered clay platelets. However, for the unweathered samples, there appears to be more regular sized hexagonal platelets (Fig. 3), while the weathered samples generally show smaller and more irregular sized and shaped platelets with some areas of fused particles (Fig. 4). The EDS results for both the unweathered and weathered clays after nonstructural iron removal are shown in Figures 5 and 6, respectively. The unweathered clay contains significant amounts of Si, Al, O, and some K (Fig. 5). Weathered specimens also show the presence of Si, Al, O, and K, but also contain Ti and Cl (Fig. 6).

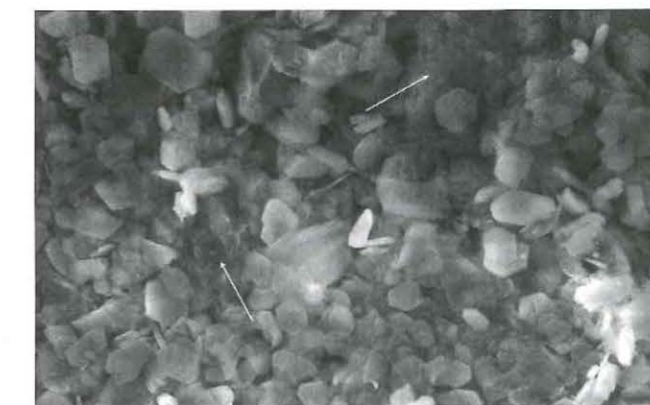


Figure 4. Electron micrograph of weathered clay after nonstructural iron removal ( $156 \mu\text{m}$  width of field).

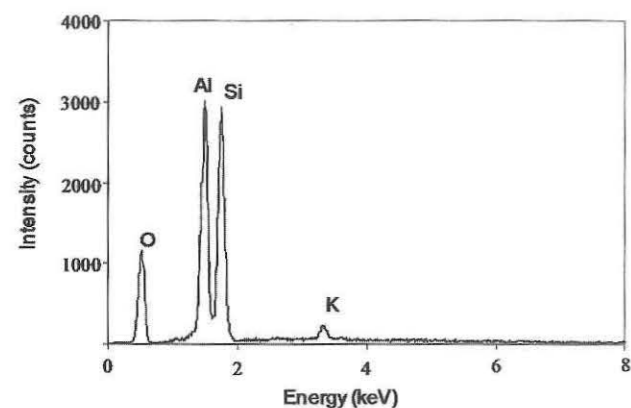


Figure 5. EDS spectrum of unweathered clay after nonstructural iron removal.

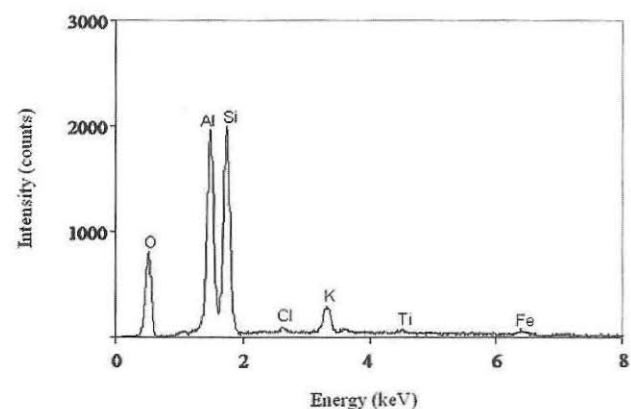


Figure 6. EDS spectrum of weathered clay after nonstructural iron removal.

To investigate the potential source of elements in the weathered specimens post-nonstructural iron treatment, ESEM was used to identify the possible presence of impurities in the clays prior to treatment. It was found that there were small amounts of other minerals observed among the clay platelets, and these exhibited brighter images by comparison with the clay particles due to their higher atomic numbers. Higher magnification images of these minerals were recorded, and the EDS results were obtained for a range of impurities. Although several types of mineral impurities were observed in the unweathered clay, their presence was minimal and they were generally small in size. The weathered clays appeared to contain a larger amount of impurities, and the particle size was increased. Based on the EDS analyses, two common types of impurities were observed in the unweathered clay. Both types contained O, Al, Si, K, and Fe, but one type also contained Na and Mg while the other also contained S. For the impurities found in the weathered clay, O, Al, Si, K, and Fe were detected, and Ti was found in addition in certain impurities.

## DISCUSSION

ESEM-EDS provides detailed information about the weathering of the cementing clay in a Sydney sandstone. The clay

samples were shown to contain loose or stacked hexagonal platelets with sizes in the 2–5  $\mu\text{m}$  range. These are typically the shapes and sizes of kaolinite clay platelets, where the preferred orientation of the basal plane (0 0 1) results in a stacking that forms book-like clay particles (Murray, 1995). Smaller clay platelets and platelets with irregular shapes appear to have been formed in the weathered samples and potentially indicate the destabilization of the aluminosilicate crystal structure. The EDS results show that the elements Fe, Ti, and Cl are included in the weathered clay.

The appearance of Fe in the aluminosilicate clay structure of clay is believed to be the result of isomorphous substitution (Malden & Meads, 1967; Farmer et al., 1971; McBride et al., 1975; Rozenson & Heller-Kallai, 1977; Komusinski et al., 1981). Iron in its ferric form ( $\text{Fe}^{3+}$ ) can replace  $\text{Al}^{3+}$  in the octahedral sites of the aluminosilicate structure. Although the two ions have equivalent charges, the ionic radius of  $\text{Fe}^{3+}$  (128 pm) is more than double of the ionic radius of  $\text{Al}^{3+}$  (50 pm). The stress introduced in the crystal lattice through substitution greatly decreases the crystallinity of the kaolinite structure in the cementing materials and may rupture the platelets. In addition,  $\text{Fe}^{3+}/\text{Al}^{3+}$ , together with  $\text{K}^+$ , can also substitute  $\text{Si}^{4+}$  in the tetrahedral sites. Although the charge balance is accommodated in this form of substitution, this phenomenon is less common due to the extra strain introduced into the crystal lattice (Meads & Malden, 1975; Hall, 1980; Petit & Decarreau, 1990). However, an increase in K concentration in the weathered clay suggests that this type of substitution has occurred upon weathering. Substitutions of any kind are likely to destabilize or destroy the crystal structure of the clay, resulting in the breakdown of its aluminosilicate layers upon weathering. The ESEM-EDS results support the findings obtained from thermal analysis, X-ray diffraction, and spectroscopy, which also provided evidence of an isomorphous substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  (Friolo et al., 2003, 2005a; Ip et al., 2008a, 2008b). It has been reported in some studies that the increase in total iron content in clay samples, particularly that of kaolinite, is associated with an exponential decrease in crystallinity of the kaolinite crystal structure with increasing time (Hinckley, 1963; Mestdagh et al., 1980; Hassan & Salem, 2002). This may indicate that a small amount of iron substituted into the crystal structure of the cementing clay could result in a significant effect on the properties of the clay.

An EDS examination of the impurities present in the clays prior to the iron removal treatment revealed that other minerals were present. Such minerals provide a potential source of the elements appearing in the weathered clay structures. The intensities of Al, Si, and O in the EDS results suggest the presence of aluminosilicate minerals. In addition, other elements such as Mg and Na indicate a mixture of several minerals or salts. The ESEM-EDS results of another mineral type observed in the unweathered cementing clay give a good indication that the observed mineral is pyrite ( $\text{FeS}_2$ ) or jarosite ( $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ ) due to the presence of Fe and S (Bell et al., 1996). There is a significant accumulation of Fe rich impurities and Ti compounds observed in

the weathered samples. Many of the impurities in the cementing clay samples are believed to originate from the sandstone or are the products of the weathering process. Iron and titanium impurities are often found in clay as hematite, siderite, pyrite, anatase, and rutile (Weaver, 1968; Maynard et al., 1969; Asmatulu, 2002). Other sources of iron may include building materials containing iron, steel roofing, water piping, and window or door frames. Given the proximity of the cathedral to the ocean, the Cl observed may be derive from the increased salt in the environment.

## CONCLUSIONS

ESEM-EDS provides structural details of the cementing clay in a Sydney heritage sandstone. Hexagonal clay platelets were observed and mineral impurities were present, particularly in the weathered clay samples. The elemental composition of unweathered and weathered clays from the sandstone indicates structural changes. Isomorphous substitution within the aluminosilicate structure, where  $\text{Fe}^{3+}$  replaces  $\text{Al}^{3+}$ , was indicated by ESEM-EDS. Other cationic substitution, such as  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  together with  $\text{K}^+$  substituting for  $\text{Si}^{4+}$  in the tetrahedral sites, may also occur.

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## REFERENCES

- ASMATULU, R. (2002). Removal of the discolouring contaminants of an East Georgia kaolin clay and its dewatering. *Turkish J Eng Environ Sci* 26, 447–453.
- BELL, E., DOWDING, P. & COOPER, T.P. (1996). Black crusts formed during two different pollution regimes. In *Processes of Urban Stone Decay: Proceedings of SWAPNET '95, Stone Weathering and Atmospheric Pollution Network Conference*, Smith, B.J. & Warke, P.A. (Eds.), pp. 47–52. London: Donhead.
- CARROLL, D. (1970). *Clay Minerals: A Guide to Their X-Ray Identification*. Boulder, CO: Geological Society of America.
- FARMER, V.C., RUSSELL, J.D., MCHARDY, W.J., NEWMAN, A.C.D., AHLRICH, J.L. & RIMSAY, J.Y.H. (1971). Evidence for loss of protons and octahedral iron from oxidised biotites and vermiculites. *Mineral Mag* 38, 121–137.
- FRIOLO, K.H., RAY, A.S., STUART, B.H. & THOMAS, P.S. (2004). Degradation of historic sandstone buildings of Sydney. In *Proceedings of the 7th Australasian Masonry Conference*, Masia, M. (Ed.), pp. 420–427. Newcastle, Australia: University of Newcastle.
- FRIOLO, K.H., RAY, A.S., STUART, B.H. & THOMAS, P.S. (2005a). Thermal analysis of heritage stones. *J Therm Anal Cal* 80, 559–563.
- FRIOLO, K.H., RAY, A.S., STUART, B.H. & THOMAS, P.S. (2005b). Investigation of the degradation of sandstones in Sydney's heritage buildings. In *Structural Analysis of Historical Constructions: Possibilities of Numerical and Experimental Techniques, Vol. 1*, Modena, C., Lourenco, P.B. & Roca, P. (Eds.), pp. 239–244. London: Taylor and Francis.
- FRIOLO, K.H., STUART, B.H. & RAY, A. (2003). Characterisation of weathering of Sydney sandstones in heritage buildings. *J Cult Her* 4, 211–220.

- HALL, P.L. (1980). The application of electron spin resonance spectroscopy to studies of clay minerals: I. Isomorphous substitutions and external surface properties. *Clay Mineral* 15, 321–335.
- HASSAN, M.S. & SALEM, S.M. (2002). Distribution and influence of iron phases on the physico-chemical properties of phyllosilicates. *Chinese J Geochem* 21, 29–39.
- HINCKLEY, D. (1963). Variability in crystallinity values among the kaolin deposits of the coastal plain of Georgia and South Carolina. *Clay Clay Miner* 2, 229–235.
- IP, K.H., STUART, B.H., RAY, A.S. & THOMAS, P.S. (2008a). A spectroscopic investigation of the weathering of a heritage Sydney sandstone. *Spectrochim Acta A* 71, 1032–1035.
- IP, K.H., STUART, B.H., THOMAS, P.S. & RAY, A.S. (2008b). Thermal characterisation of the clay binder in heritage Sydney sandstones. *J Therm Anal Cal* 92, 97–100.
- KOMUSINSKI, J., STOCH, L. & DUBIEL, S.M. (1981). Application of electron paramagnetic resonance and Mössbauer spectroscopy in the investigation of kaolinite-group minerals. *Clay Clay Miner* 29, 23–30.
- MALDEN, P.J. & MEADS, R.E. (1967). Substitution by iron in kaolinite. *Nature* 215, 844–846.
- MAYNARD, R.N., MILLMAN, N. & IANNICELLI, J. (1969). A method for removing titanium dioxide impurities from kaolin. *Clay Clay Miner* 17, 59–62.
- MCBRIDE, M.B., PINNAVAIA, T.J. & MORTLAND, M.M. (1975). Perturbation of structural  $\text{Fe}^{3+}$  in smectites by exchange ions. *Clay Clay Miner* 23, 103–107.
- MCNALLY, G.H. & FRANKLIN, B.J. (2000). *Sandstone City—Sydney's Dimension Stone and Other Sandstone Geomaterials*. Sydney: Geological Society of Australia.
- MEADS, R.E. & MALDEN, P.J. (1975). Electron spin resonance in natural kaolinites containing  $\text{Fe}^{3+}$  and other transition metal ions. *Clay Miner* 10, 313–345.
- MEHRA, O.P. & JACKSON, M.L. (1960). Iron oxides removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. *Clay Clay Miner* 7, 317–327.
- MESTDAGH, M.M., VIELVOYE, L. & HERBILLON, A.J. (1980). Iron in kaolinite: II. The relationship between kaolinite crystallinity and iron content. *Clay Miner* 15, 1–13.
- MURRAY, H.H. (1995). Clays in industry and the environment. In *Proceedings of the 10th International Clays Conference*, Churchman, G.J., Fitzpatrick, R.W. & Eggleton, R.A. (Eds.), pp. 49–55. Melbourne: CSIRO Publishing.
- PETIT, S. & DECARREAU, A. (1990). Hydrothermal (200°C) synthesis and crystal chemistry of iron-rich kaolinites. *Clay Miner* 25, 181–196.
- ROSCOE, R., BURMAN, P. & VELTHORST, E.J. (2000). Disruption of soil aggregates by varied amounts of ultrasonic energy in fractionation of organic matter of a clay latosol: Carbon, nitrogen and  $\delta^{13}\text{C}$  distribution in particle-size fractions. *Eur J Soil Sci* 51, 445–454.
- ROZENSON, I. & HELLER-KALLAI, L. (1977). Mössbauer spectra of dioctahedral smectites. *Clay Clay Miner* 25, 94–101.
- RUTLEDGE, E.M., WILDING, L.P. & ELFIELD, M. (1967). Automated particle-size separation by sedimentation. *Proc Soil Sci Soc Amer* 31, 287–288.
- SCHMIDT, M.W., RUMPEL, C. & KOGEL-KNABNER, I. (1999). Evaluation of an ultrasonic dispersion procedure to isolate primary organomineral complexes from soils. *Eur J Soil Sci* 50, 87–94.
- WEAVER, C.E. (1968). Electron microprobe study of kaolin. *Clay Clay Miner* 16, 187–189.