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Use of strontium isotopes to determine the origin of cement in concretes Case examples from New Zealand

I.J. Graham[a,*], R.L. Goguel[b], D.A. St John[b]

[a]Institute of Geological and Nuclear Sciences, PO Box 31312, Lower Hutt, New Zealand
[b]Industrial Research Ltd., PO Box 31310, Lower Hutt, New Zealand

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Abstract

Combined chemical and strontium isotopic analysis has shown that New Zealand cements carry geochemical fingerprints from their raw materials, which can be used to identify them in concrete. This could prove to have a more general application in tracing the origin of cement and identifying the causes of failure in concrete structures. The fingerprinting of cement in concrete is complicated by aggregate leaching, but this can be minimised by using slightly alkaline or neutral EDTA as the solvent in preference to weak mineral acids such as HNO_3. Although fingerprinting of most New Zealand cements is possible, based on the relative concentrations of Ca, Sr, and Mn, strontium isotopes can add crucial information in certain cases, particularly where limestones of contrasting geological ages have been used as raw materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cement; Concrete; Fingerprinting; Strontium isotopes; Aggregate

1. Introduction

Analytical methods designed to identify the manufacturing source of cement in concrete have not been widely developed. In many countries, including New Zealand, government agencies carry out regular analytical checks on cement production, and the analytical data so obtained can prove useful when investigating the durability or failure of public structures, providing that unequivocal identification of the mix of materials in the concretes were possible. The investigation of alkali aggregate reaction in concrete is of particular interest in this respect. However, in New Zealand, records of the materials used and of mix design are no longer available for most structures, and reliable analytical methods for determining directly alkali contents in hardened concrete are still being developed [1].

Cement in New Zealand is usually manufactured from local materials (i.e. limestone, shale, marl) and only gypsum is imported, the source being dictated by economic factors. Manufacturers control the cement composition to narrow tolerances, and the final composition is largely dictated by the raw materials available and the manufacturing processes used. Thus, in New Zealand, the composition of cements from individual works has varied minimally with time [2] (Table 1). There are, however, sufficient compositional differences between the various cements to allow positive identification (fingerprinting) using a range of elemental concentrations and ratios, [cf. Refs. [2–4] and potentially, isotopes. To be useful for fingerprinting, these compositional characteristics would have to be preserved in concrete under a wide range of environmental conditions for periods of up to 50 years. In particular, any interaction between pore solutions in the concrete and the aggregates used would have to be minimal.

In a previous investigation, Goguel and St John [2,3] determined major and trace element concentrations in four widely used New Zealand cements (Foulwind, Tarakohe, Portland (Whangarei) and Burnside; Fig. 1) and two less widely used cements (Waitomo and Southland). They established that these could be satisfactorily distinguished from their Ca, Mn, and Sr contents and Ca/Sr. Here, we have used several of their samples to investigate the suitability of Sr isotopes to provide additional evidence that might prove useful where chemical parameters leave a degree of ambiguity.

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* Corresponding author. Tel.: +64-4-5704-677; fax: +64-4-5704-657.
E-mail address: i.graham@gns.cri.nz (I.J. Graham).

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Table 1
Ca, Sr contents, and Sr isotopic compositions of New Zealand cement manufactured after 1950

Sample	Cat.no.[a]	Date	Ca (wt.%)	Sr (wt.%)	Ca/Sr	$^{87}Sr/^{86}Sr$ (p)[b]
Foulwind						
Foul-62	14643	1962	42.00	0.0248	1694	0.71197 (0.00005)
Foul-71	14644	1971	47.70	0.0335	1424	0.71103 (0.00003)
S3	14406	1972	47.28	0.0280	1689	0.71111 (0.00007)
Foul-78A	14645	1978	48.60	0.0315	1543	0.71070 (0.00004)
Foul-78B	14646	1978	47.00	0.0288	1632	0.71084 (0.00006)
Foul-83A	14647	1983	47.70	0.0338	1411	0.71077 (0.00011)
Foul-83B	14648	1983	46.50	0.0372	1250	0.71077 (0.00005)
Tarakohe						
T1	15969	1952	43.42	0.0593	732	0.70760 (0.00005)
T2	15970	1963	45.05	0.0611	737	0.70777 (0.00004)
T3	15971	1965	35.74	0.0595	601	0.70801 (0.00007)
T4	15972	1968	39.18	0.0564	595	0.70798 (0.00005)
T5	15973	1972	45.13	0.0720	627	0.70796 (0.00004)
S1	14400	1972	48.17	0.0628	767	0.70797 (0.00004)
T6	15974	1988	46.54	0.0688	676	0.70773 (0.00004)
Portland						
P1	17235	1962	48.58	0.1895	256	0.70819 (0.00006)
P2	17236	1963	42.37	0.1420	298	0.70824 (0.00005)
P3	17237	1964	39.80	0.1400	284	0.70828 (0.00007)
P4	17238	1966	37.94	0.1440	263	0.70817 (0.00006)
P5[c]	17239	1970	48.59	0.1285	378	0.70822 (0.00004)
P6	17240	1972	39.82	0.0862	462	0.70821 (0.00007)
S2[c]	14401	1972	49.05	0.1547	317	0.70816 (0.00004)
P7	17241	1982	43.34	0.1398	312	0.70815 (0.00006)
P8	17242	1988	47.46	0.1754	271	0.70803 (0.00005)
P9	17243	1989	48.06	0.1815	265	0.70811 (0.00005)
Waitomo						
W2	17244	1962	46.90	0.1002	468	0.70813 (0.00007)
S4	14402	1968	45.74	0.0730	627	0.70793 (0.00004)
Burnside						
S5[c]	14404	1975	47.53	0.0497	956	0.70862 (0.00004)
Southland						
S6	14403	1955/65	46.39	0.1116	266	0.70832 (0.00005)
Fiji						
S7	14405	1972	45.53	0.4928	92	0.70910 (0.00005)

[a] Institute of Geological and Nuclear Sciences petrology collection.

[b] p is 2σ precision.

[c] Rapid hardening (all others ordinary).

2. Analytical methods

For successful chemical fingerprinting of cement in concrete, it is important to leach the cement without significantly attacking the aggregate. As with previous studies of this type [2,3], dilute HNO_3 was used here since this acid extracts less from the aggregates than picric acid/methanol mixtures [1]. However, it does not discriminate as well for Sr or Ca as alkaline or neutral EDTA, which barely attacks the aggregate at all [6].

Bulk cement and aggregates were digested in a mixture of $HF-HClO_4$ and then taken up in 0.2 M HNO_3. The final solutions contained about 27.5 wt.% cement. Representative concrete samples of about 250 g were prepared for leaching by drying thoroughly at 105°C, crushing in a mortar and collecting the 0.5–1.0 mm fraction by sieving. About 0.5 g of the sieved fraction was then shaken for 1 h at room temperature in excess 1.0 M HNO_3 or 0.2 M NH_4 EDTA at pH 7, the solution was separated by centrifuging and the clear liquid decanted off. Sr and Ca analysis was undertaken using ICP-AES [2]. Strontium for isotopic analysis was extracted using standard cation exchange techniques [7], and analysed on a VG MM30B mass spectrometer at the Institute of Geological and Nuclear Sciences (GNS), Lower Hutt, New Zealand, and a VG Sector 54E instrument at the Centre for Isotope Studies, CSIRO, Sydney, Australia (R16988 and R16989). $^{87}Sr/^{86}Sr$ was adjusted to $^{86}Sr/^{88}Sr = 0.1194$ and final results normalised to an SRM987 value of 0.71025, the mean for both instruments over the previous 5 years.

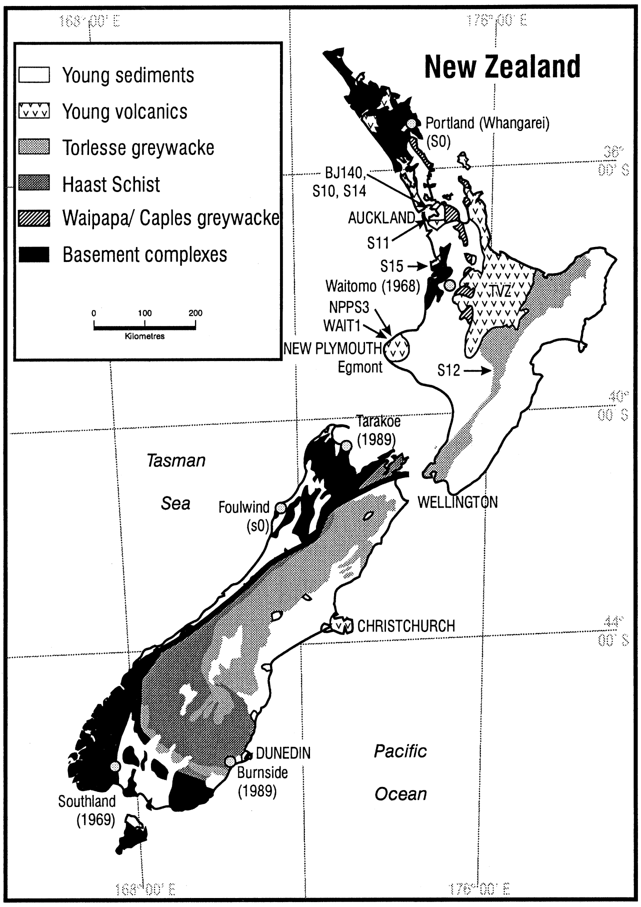

Fig. 1. Location of New Zealand cement works and concrete structures sampled for this study, and the distribution of the main lithologies used as concrete aggregate [5]. The numbers in brackets indicate the date of works closure (SO = still operating).

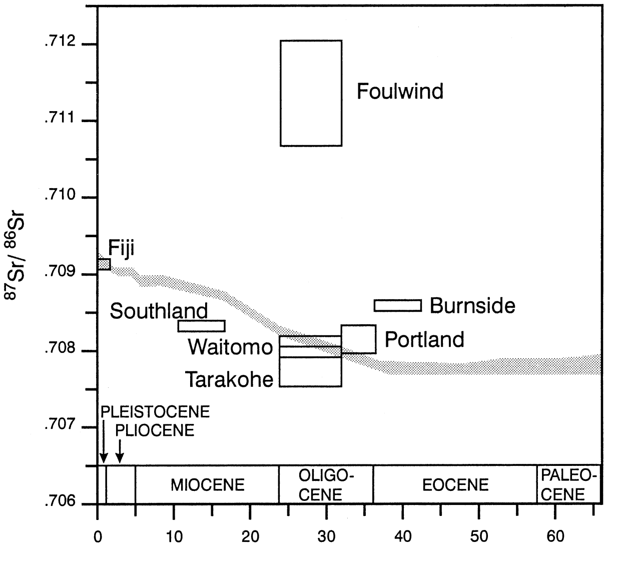

Fig. 2. ^{87}Sr/^{86}Sr of New Zealand and Fiji cements plotted against the Cretaceous–Tertiary paleo-seawater curve [8], from which the main constituent limestones derive their Sr isotopic compositions.

3. Results and discussion

3.1. Cement compositions

Strontium isotope ratios for the New Zealand cements analysed in this study range from 0.7076 to 0.7120 (Table 1), with most being close to 0.7080 (Fig. 2). With the exception of Foulwind and Burnside cement, ^{87}Sr/^{86}Sr values are similar to those of their constituent limestones, mainly mid-Tertiary, Oligocene–Miocene deposits (Fig. 2). Foulwind and Burnside cements have the lowest Sr contents (Table 1) and their ^{87}Sr/^{86}Sr values have thus been more affected by Sr contained in impurities. Foulwind cement, in particular, has ^{87}Sr/^{86}Sr much higher than Oligocene limestone due to the presence of a very radiogenic clay in the limestone (Table 2). This has resulted in the cement showing significant variation in ^{87}Sr/^{86}Sr throughout the last 30 years of manufacture (Table 1), the major changes occurring in 1962 and 1972 when new quarry faces were opened up. However, since 1962, variation has been relatively small and not sufficient to allow any confusion with the other cements analysed. Generally, high Sr contents in the cement should provide a buffer against significant variation in ^{87}Sr/^{86}Sr. Tarakohe (0.7076–0.7081) and Portland (0.7080–0.70835) cements, by comparison, show only minor variations over the same time period. One important variant is gypsum of which approximately 5 wt.% is added to the final clinker before crushing. An Australian-sourced gypsum which was added to New Zealand cements up to 1989 has a very high Sr content (Table 2) which has had a significant effect on ^{87}Sr/^{86}Sr, particularly when coupled with low Sr content. In this regard, a 1990 change to Thailand-sourced gypsum at Foulwind will have a marked effect on future cement compositions there.

Overall, there are measurable differences in the mean ^{87}Sr/^{86}Sr of most of the cements analysed, which can be used to fingerprint them. Waitomo and Southland cements have non-unique ^{87}Sr/^{86}Sr, and are not easily distinguished from Tarakohe and Portland cements, respectively, even when Ca/Sr is taken into account (Fig. 3). A currently manufactured cement from Fiji (Table 1) which uses coral as its main raw material has very high Sr (ca. 0.49 wt.%) and is distinguishable from all the New Zealand cements on the basis of both ^{87}Sr/^{86}Sr (Fig. 2) and Ca/Sr (Fig. 3).

3.2. Aggregate compositions

Four main types of aggregate are used in more than 90% of New Zealand concretes: Taupo Volcanic Zone (TVZ) rhyolite–ignimbrite, Egmont andesite, Auckland basalt, and greywacke. In addition, a number of other aggregates such as TVZ and Coromandel andesite and Dunedin phonolite are used locally (see Fig. 1 for distribution of these lithological groups in New Zealand). Some of the above aggregate types are contained in the specific concrete samples analysed for this study, and their mean Ca and Sr contents and ^{87}Sr/^{86}Sr range widely (Table 3). Auckland basalt is very localised but is used widely in the Auckland region (the most populous urban area in New Zealand). The rocks have relatively low ^{87}Sr/^{86}Sr (0.7026–0.7042), and

Table 2
Ca, Sr contents, and strontium isotopic compositions of Foulwind cement ingredients

	Cat. no.	Ca (wt.%)	Sr (wt.%)	Ca/Sr	^{87}Sr/^{86}Sr
High Mn clay	15093	0.65	0.0011	591	0.72296 (0.00007)
Blue bottom clay	15094	1.15	0.0021	548	0.70995 (0.00005)
Marl	15095	17.2	0.0268	642	0.71089 (0.00005)
Impure limestone	15096	40.8	0.0130	3138	0.71181 (0.00007)
Third incline limestone	15097	39.4	0.0167	2383	0.71043 (0.00007)
North heading limestone	15098	40.1	0.0171	2345	0.71072 (0.00006)
Pacific limestone	15099	39.6	0.0178	2225	0.71039 (0.00003)
Australian gypsum	14649	28.4	0.2806	101	0.70943 (0.00006)
Thailand gypsum	14650	23.8	0.0430	553	0.70838 (0.00005)

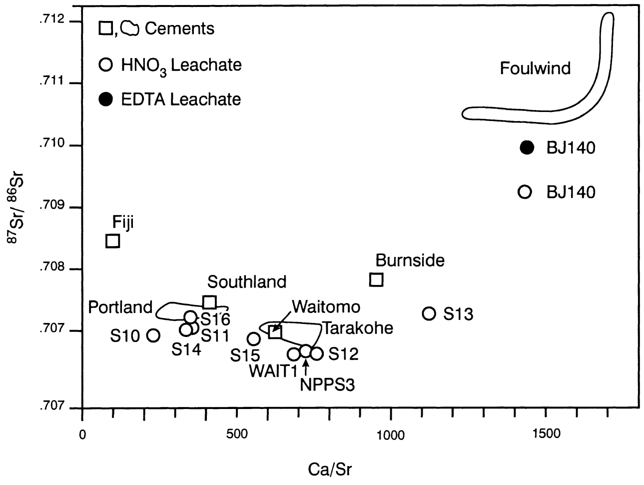

Fig. 3. $^{87}Sr/^{86}Sr$ vs. Ca/Sr for New Zealand cements, concretes and test cores. Fields are given for Foulwind, Tarakohe, and Portland cements (See Table 1).

high Sr (0.03–0.10 wt.%). Egmont andesite is also very localised and, although Ca and Sr contents are similar to Auckland basalt, $^{87}Sr/^{86}Sr$ is significantly higher (0.7044–0.7048). Rhyolite–ignimbrite is widespread in the TVZ and has generally lower Sr (0.01 to 0.02 wt%) and higher $^{87}Sr/^{86}Sr$ (0.7048 to 0.7061) than the other volcanic aggregates described above. Torlesse and Waipapa/Caples greywacke (and their Haast Schist equivalents) are distributed widely throughout New Zealand, comprising the main ranges of both islands. Greywacke river gravel is the major aggregate type used in the South Island. Both its Sr content (0.015–0.060 wt.%) and $^{87}Sr/^{86}Sr$ (0.703 to 0.710) vary widely (Table 3).

Because of this wide variation of both Sr content and $^{87}Sr/^{86}Sr$ of New Zealand concrete aggregates, it was necessary to analyse a selection of clast types in individual concretes to properly assess the possible effects of aggregate contamination on the cement leachate.

Goguel and St John [3] undertook controlled experiments on the main aggregate types to determine the effects of leachate contamination. Drilled cores and crushed fractions, the latter representing more accurately the fine aggregate present in concrete, were subjected to similar leaching conditions to those of the concrete samples (see Analytical methods). Under these experimental conditions, only Si and Ba approach a limit of solubility and none of the main mineral phases except quartz are stable. Strontium contributions to the leachate are typically low, especially if EDTA is used rather than HNO_3, and are highest from greywacke, generally from the fine (<0.125 mm) crushed fraction. Auckland basalt aggregate yielded particularly high Sr contributions for 1.0 M HNO_3, reinforcing the need for alkaline leaching of the concrete samples where this aggregate is used.

3.3. *Concrete investigations*

Several concrete samples from old structures plus a laboratory prepared sample were analysed to test the validity of the $^{87}Sr/^{86}Sr$ fingerprinting method, yielding the following results.

3.3.1. *Pahurehure Bridge, Auckland (BJ140)*

Pahurehure inlet bridge deck beams were constructed in 1964. Petrographic examination shows that the concrete contains about 400 kg/m^3 of cement with a water:cement ratio (W/C) of 0.5, Auckland basalt as coarse aggregate and crusher dust, together with Waikato River sand containing mixed rhyolite–ignimbrite and andesite volcanic clasts. Sr isotopic analysis of both HNO_3 and EDTA leachates indicates that Foulwind cement was used, a result consistent with chemical identification [2,3]. The Sr isotopic compositions of both leachates, particularly the less discriminating HNO_3, are lower than that of Foulwind cement manufactured in 1964 (Fig. 4), because of the unfavourably high Sr content (ca. 0.06 wt.%) and low $^{87}Sr/^{86}Sr$ (0.70361; Table 5) of the aggregate. However, there is no doubt as to the identification of the cement even when HNO_3 is used to extract the Sr (Fig. 3).

3.3.2. *Waitara Bridge, New Plymouth (WAIT1)*

The Waitara River Bridge was constructed in 1982. Cores from an abutment and wing wall contain 290 kg/m^3 of cement, believed to be Tarakohe. Petrographic examination indicates that Egmont andesite derived from alluvial sources was used as aggregate. The $^{87}Sr/^{86}Sr$ of the HNO_3

Table 3
Mean Ca, Sr contents, and strontium isotopic compositions of the main New Zealand concrete aggregate types
TVZ = Taupo Volcanic Zone; unp = unpublished data; Σ = number of samples in mean.

	References	Ca [wt.% (*p*)]	Sr [wt.% (*p*)]	Ca/Sr (*p*)	Σ	$^{87}Sr/^{86}Sr$ (*p*)	Σ
Auckland basalt	[9], unp	7.11 (1.03)	0.064 (0.037)	111 (51)	46	0.7034 (0.0008)	4
Egmont basalt	[10]	6.41 (1.62)	0.066 (0.011)	97 (49)	8	0.7046 (0.0002)	12
TVZ andesite	[11,12], unp	5.13 (2.35)	0.029 (0.020)	177 (654)	332	0.7052 (0.0010)	252
TVZ rhyolite	unp	1.17 (0.65)	0.013 (0.06)	90 (170)	36	0.7055 (0.0007)	26
Torlesse greywacke	[7,13,14], unp	1.24 (0.86)	0.031 (0.015)	40 (91)	26	0.7106 (0.0039)	101
Waipapa/Caples greywacke	[15], unp	2.74 (0.58)	0.046 (0.017)	60 (54)	8	0.7059 (0.0032)	33
Dunedin phonolite	[16,17]	0.97 (1.34)	0.020 (0.040)	49 (–)	5	0.7115 (0.0093)	8

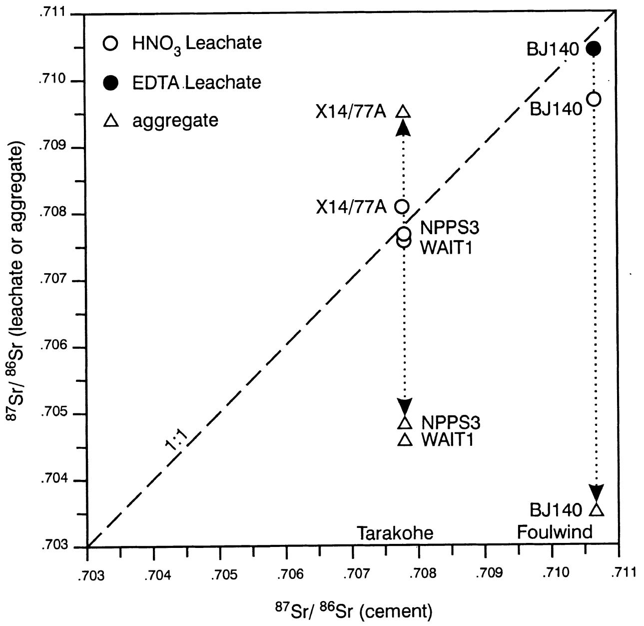

Fig. 4. $^{87}Sr/^{86}Sr$ of cement leachates or aggregates vs. $^{87}Sr/^{86}Sr$ of corresponding cements for selected New Zealand concretes and test cores. Small contributions from the aggregate draw the leachate compositions away from the 1:1 line.

leachate is only slightly lower than that of Tarakohe cement, having been modified possibly by a small Sr contribution from the aggregate (Fig. 4). However the relatively low $^{87}Sr/^{86}Sr$ of the andesite aggregate in this concrete (0.70469; Table 5) compared with Auckland basalt, coupled with the higher Sr content of the cement makes the effects of aggregate contamination much less than for Pahurehure Bridge concrete.

3.3.3. New Plymouth Power Station (NPPS3)

Constructed in 1970, the New Plymouth Power Station used concrete of similar specification to that of the Waitara River Bridge and thus yields similar results (Figs. 3 and 4).

3.3.4. Whenuapai Airbase, Auckland (S10 and S14)

Constructed in 1963/64, the pavement for the Whenuapai Airbase was placed in two parts, both containing 330 kg/m^3 of cement at W/C = 0.5. Sample S10 is from an area in which the concrete contains Auckland basalt as coarse aggregate (and crusher dust) together with Waikato River sand, while S14 is from an area in which the concrete contains Auckland basalt as coarse aggregate together with marine sand consisting primarily of quartz, feldspar, minor mafics and shell fragments. Leachates of both samples have

Table 4
Ca/Sr ratios and strontium isotopic compositions of concrete test sample leachates
? = unknown or assumed.

					Leachate	
Structure	Date	Sample	Aggregate	Cement[a]	Ca/Sr	$^{87}Sr/^{86}Sr$ (p)
Pahurehure Bridge	1963	BJ140 15105	Auckland basalt + Waikato river sand[b]	Unknown (Foulwind)	1440	0.70976 (0.00003) 0.71043 (0.00006)[c]
Waitara Bridge	1982	WAIT1 15104	Egmont andesite	Tarakohe? (Tarakohe)	688	0.70768 (0.00007)
NP Power Station	1970	NPPS3 15103	Egmont Andesite	Tarakohe? (Tarakohe)	730	0.70773 (0.00007)
Whenuapai Airfield	1964	S10 16183	Auckland basalt + Waikato sand	Unknown (Portland)	234	0.70791 (0.00006)
		S14 16187	Auckland basalt + beach sand[d]		335	0.70798 (0.00004)
Waitomo Quarry shed	1960	S15 16188	Local limestone	Waitomo (Waitomo)	558	0.70787 (0.00003)
Mangahuia Bridge	?	S12 16185	Egmont andesite?	Tarakohe? (Tarakohe)	752	0.70767 (0.00004)
NZ Steel wall	1983	S11 16184	Auckland basalt + Waikato river sand[b]	Portland? (Portland)	350	0.70800 (0.00004)
Lab. test cylinder 1	?	S13 16186	Dunedin phonolite	Burnside? (Burnside)	1123	0.70818 (0.00004)
Lab. test cylinder 2	1991	S16 16189	Auckland basalt + Waikato river sand[b]	Portland (Portland)	343	0.70813 (0.00005)
Lab. test cylinder 3	1987	S190 14642	Auckland basalt + quartz sand	Foulwind (Foulwind)	–	0.70972 (0.00004)
Lab. test cylinder 4	1974	X14/77A 15106	Torlesse greywacke	Tarakohe (Tarakohe)	–	0.70809 (0.00004)

[a] Original identification first; chemical/isotopic identification in brackets.
[b] Quartz + TVZ volcanics + Waipapa greywacke.
[c] EDTA extraction (all others 1.0 M HNO_3 extraction).
[d] Quartz + feldspar.

Table 5
Strontium isotopic composition of concrete clasts, concrete mortars, and fly-ash

Sample	Origin	Cement	Ca/Sr	$^{87}Sr/^{86}Sr$ (p)
Concrete clasts				
BJ140 15105c	Auckland basalt	Foulwind 1964	–	0.70361 (0.00006)
WAIT1 15104c	Egmont andesite	Tarakohe 1962	–	0.70469 (0.00005)
NPPS3 15103c	Egmont andesite	Tarakoe 1970	–	0.70495 (0.00006)
X14/77A 15106c	Torlesse greywacke	Tarakohe 1974	–	0.70963 (0.00005)
Concrete mortars				
1 15107	Auckland basalt	Foulwind 1987	–	0.70353 (0.00005)
9 15108	Auckland basalt	Tarakohe (high alkali)	–	0.70366 (0.00006)
Fly-ashes				
FA1 16988	Huntly coal	–	67	0.70613 (0.00001)
FA2 16989	Huntly coal	–	34	0.70643 (0.00001)

identical $^{87}Sr/^{86}Sr$, close to that of Portland cement (Fig. 3), in agreement with the chemical identification [2,3].

3.3.5. Waitomo quarry shed (S15)

A shed constructed at the Waitomo limestone quarry in 1960 used the local limestone as aggregate. The $^{87}Sr/^{86}Sr$ of the extracted leachate is similar to the 1968 Waitomo cement (Fig. 3) but slightly lower than the 1962 cement (Table 1). This, despite the aggregate being the same as the main constituent of the cement, and therefore, having minimal effect on the composition of the leachate.

3.3.6. Mangahuia Bridge, New Plymouth (S12)

Mangahuia Bridge was constructed with Egmont andesite at a time unknown. The $^{87}Sr/^{86}Sr$ of the extracted leachate is similar to other Taranaki structures which used Tarakohe cement.

3.3.7. NZ steel concrete wall, Auckland (S11)

A concrete wall, constructed at the NZ Steel works, Glenbrook in 1983, used Auckland basalt as coarse aggregate together with Waikato River sand and basalt crusher dust. The $^{87}Sr/^{86}Sr$ of the extracted leachate indicates the use of Portland (Whangarei) cement (Fig. 3), in agreement with the chemical identification [2,3].

3.3.8. Test cylinders

Various laboratory-prepared test cylinders with a variety of cement and aggregate types were analysed (Table 4), and all yielded predictable Sr isotopic results (Fig. 3). For Test Core X14/77A, the aggregate (Torlesse greywacke) has a higher $^{87}Sr/^{86}Sr$ than the cement causing the HNO_3 leachate to increase slightly above its expected value (Fig. 4). However, the relatively low Sr content of the greywacke (ca. 250 mg/kg) has meant that the shift was lower than that caused by andesite or basalt aggregates.

3.4. Use of fly-ash

When aggregates are used that are subject to deleterious reaction with the highly alkaline pore solutions of concrete, part of the cement (ca. 25%) is commonly replaced by fly-ash from coal burning plants. Fly-ash reduces the alkalinity of the pore solutions, and is only available in New Zealand from the Huntly coal-fired power station south of Auckland (Fig. 1). Strontium contents of the fly-ash (0.02–0.05 wt.%) are similar or lower than those of the cements used, and Ca contents (1.4–1.6 wt.%) are much lower (cf. Table 1). Consequently, use of fly-ash has a major effect on Ca/Sr of the cement, limiting the future use of that ratio for identification purposes. The relatively low $^{87}Sr/^{86}Sr$ of the fly-ash (ca. 0.7062; Table 5) will also lower the $^{87}Sr/^{86}Sr$ of the cement, but this effect is somewhat buffered by the typically lower Sr content of the fly-ash. Hence, if the presence of fly-ash is not recognised in a cement mix, erroneously low Ca/Sr and $^{87}Sr/^{86}Sr$ will be determined, hampering accurate future identification.

4. Summary and conclusions

Combined chemical and Sr isotopic analysis of commonly used New Zealand cements has shown that they contain characteristic fingerprints, which may be used to identify them in concrete of unknown origin. Although the cements have typically $^{87}Sr/^{86}Sr$ values similar to their mid-

Tertiary limestone source rocks (0.7078–0.7085), most are easily distinguishable when their $^{87}Sr/^{86}Sr$ values are plotted against Ca/Sr. Most of the cements have been manufactured from relatively "pure" raw materials with high Sr contents (0.05–0.17 wt.%) so are buffered against major changes in either $^{87}Sr/^{86}Sr$ or Ca/Sr with time. Leaching of cement from hardened concretes using dilute HNO_3 can generally reproduce the chemical and isotopic characteristics of the cement to acceptable tolerances, but alkaline or neutral EDTA improves the results markedly and should be used for Sr and Ca extraction where there are high compositional gradients between the cement and the aggregate, or when the aggregate is particularly susceptible to leaching.

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