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Energy and Environment Division

Retort Water Particulates

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RETORT WATER PARTICULATES

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Retort water may contain three types of suspended matter: oils and tars, raw and spent shale particles and a finely divided residue generally believed to be bacterial cells.[1] These particulates result in an extremely heterogeneous sample and complicate chemical analyses. Physical and chemical interactions between the retort water and these particulates, including mineral dissolution (from the spent shale particles), adsorption on the bacterial cells and oil-water solubility reactions can alter the composition of the dissolved fraction during sample storage.

The heterogeneity of unfiltered waters complicates chemical analysis. The coefficient of variation for replicate analyses may range from 20% to over 100% for many waters for analytical techniques that typically yield 10% precision. Therefore, a series of these waters was filtered to determine if this would produce a homogeneous sample that was not significantly altered in chemical composition from the original sample. Filtration of the first water produced a high density of crystals, about 50 to 100 μm in length, on the surface of the filter paper. Preliminary analyses of the particulate and dissolved fraction of the water suggested that a significant fraction of the dissolved constituents in the retort water could be removed by crystal formation. This startling result led to a more detailed investigation of the nature and origin of retort water particulates. This investigation and its results are discussed here.

EXPERIMENTAL

Eleven retort waters from Laramie Energy Technology Center's controlled-state retort were filtered, and the particulate fraction and the filtered water collected and analyzed for 17 elements by energy-dispersive x-ray fluorescence spectrometry (XRF). Retort operating conditions for these 11 waters are summarized in Table 1.

A 47-mm Millipore glass vacuum system with a fritted glass support screen and Millipore type HA 0.45 μm filter paper were used to collect particulates because they produced a uniform deposit of suspended material with a minimum of paper wrinkling. Tared filters were washed to remove readily soluble copper, iron, nickel, and zinc by filtering 100 ml of 0.06 M NH_4HCO_3 followed by 250 ml distilled water prior to filtration of the sample. The glass frit was moistened with distilled water before placing the filter

Table 1. RETORT OPERATING CONDITIONS FOR LETC'S CONTROLLED-STATE RETORT

Run	Shale Type	Run Type[a]	Shale grade (liters/ tonne)	Shale size range (mm)	Oil yield,% Fischer assay (volume basis)	Isothermal advance rate (m/day)	Maximum Temp. (°C)	Sweep Gas	Gas flow rate, standard m^3/m^2 min
CS-60	Colorado	I	123	3-13	46	1.83	540	100% N_2	0.12
CS-62	Utah	C	126	3-13	95	1.83	540	100% N_2	0.12
CS-63	Antrim	C	40	3-13	77	1.83	540	100% N_2	0.12
CS-64	Colorado	C	248	3-13	94	1.83	540	100% N_2	0.12
CS-65	Moroccan	C	79	3-13	88	1.83	540	100% N_2	0.12
CS-66	Colorado	C	128	3-13	91	1.83	540	75% N_2 25% steam	0.15
CS-67	Colorado	C	231	3-13	100	1.83	540	75% N_2 25% steam	0.15
CS-68	Colorado	C	119	3-13	97	1.83	540	100% N_2	0.12
CS-69	Colorado	C	118	3-13	98	1.83	760	64.5% N_2 25% steam 10.5% O_2	0.15
CS-70	Colorado	C	134	3-13	96	1.83	540	75% N_2 25% steam	0.15
CS-71	Utah	C	137	3-13	91	1.83	540	75% N_2 25% steam	0.15

[a] C = Completed run; I = Interrupted run.

paper on it to prevent wrinkling during filtration. All glassware and sample bottles were washed with soap and water, rinsed with distilled water, soaked for a minimum of 12 hours in 5 N HCl, again rinsed with distilled water, dried in an 80° C oven for 4 hours and brought to room temperature before use. In addition, the glass support screen, on removal from the acid bath, was further washed by filtering 200 ml of 5 N HCl followed by 200 ml of distilled water.

The samples were removed from a 4° C refrigerator 24 hours before analysis to bring them to room temperature and shaken for 30 sec immediately before filtration. If excessive outgassing or foaming occurred, the samples were allowed to stabilize before withdrawing a sample. A sample volume sufficient to give a particulate unit mass of about 1 mg/cm^2 (5 to 25 ml) was transferred to a filtration funnel with a Pyrex pipette and filtered by vacuum at a rate of about 1 ml/sec. The filtrate was transferred to a polyethylene container and the filter paper containing the particulates was placed in a plastic petri dish in a dessicator under silica gel. The filter papers were weighed daily until a constant weight within 2% was obtained (this typically took 2 days). Two replicates of each sample were prepared in this way. The filtrate from one replicate was stored at 4° C. The filtrate from the other replicate was left at room temperature for 15 to 17 days and refiltered to investigate the effect of bacterial growth on soluble metal content. Four blanks were carried through the entire procedure.

The abundance of 17 elements was measured by energy-dispersive x-ray fluorescence spectrometry. The instrumental method has been previously described.[2] The filter paper containing the particulates was cut into 2.5 cm discs and counted for 20 or 40 min. Filtered retort waters were prepared by pipetting seven 4-μl drops of sample onto a 0.006 mm polypropylene film tightly stretched in a plastic ring. Drop location was controlled with a jig designed to produce seven concentric spots. These deposits were air dried and the samples counted for 2000 sec. Chromium was determined by neutron activation analysis,[3] and mercury was determined by Zeeman atomic absorption spectroscopy.[4] X-ray diffraction was used to identify mineral phases. Crystals were collected with tweezers under an optical microscope and adhered to a glass rod with silicon grease. A powder pattern was taken using copper Kα radiation with a nickel filter in the beam. The morphology and chemical composition of individual particles were studied using a scanning electron microscope (Advanced Metals Research Model 1000 A) equipped with an energy-dispersive XRF analyzer (EDAX).

RESULTS AND DISCUSSION

Particulate Composition

The elemental composition of the particulates and the filtered waters and the percent of the total elemental mass associated with the particulates are summarized in Table 2. This summary shows that the major elements (>0.1 mg/l) in the particulate fraction are iron, nickel, potassium, and calcium. All other measured constituents typically occur at less than 50 μg/l. The fraction of the total elemental mass present in the particulates (% particulate) is typically less than, or about, 1% for potassium, arsenic, selenium,

Table 2. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES AND FILTERED RETORT WATERS FROM THE CONTROLLED-STATE RETORT (mg/ℓ)

Element	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Element
	CS-60			CS-62			CS-63			
Ti	<0.60	<0.053	-	<0.60	<0.056	-	0.69 ± 0.40	0.030 ± 0.011	4	Ti
V	<0.42	<0.037	-	<0.42	<0.040	-	0.49 ± 0.28	<.040		V
Cr	1.74 ± 0.22	0.15 ± 0.02	8	0.57 ± 0.01[a]	0.43 ± 0.02	43	0.09 ± 0.01[a]	0.058 ± 0.006	39	Cr
Mn	0.23 ± 0.16	0.03 ± 0.01	14	<0.21	0.065 ± 0.018	-	0.31 ± 0.14	0.022 ± 0.005	7	Mn
Fe	19.2 ± 0.9	4.32 ± 0.21	18	6.60 ± 0.33	8.73 ± 1.35	57	1.30 ± 0.14	1.43 ± 0.07	52	Fe
Ni	2.06 ± 0.10	3.38 ± 0.16	62	1.34 ± 0.08	9.32 ± 0.14	87	0.98 ± 0.08	0.031 ± 0.003	3	Ni
Ga	0.05 ± 0.04	<0.006	<11	0.06 ± 0.04	<0.006	<9	0.06 ± 0.04	<0.003	<5	Ga
As	6.04 ± 0.30	0.12 ± 0.01	2	6.22 ± 0.31	0.130 ± 0.006	2	1.82 ± 0.09	0.016 ± 0.002	1	As
Se	0.37 ± 0.04	0.032 ± 0.004	8	0.47 ± 0.04	0.043 ± 0.004	8	0.51 ± 0.04	0.004 ± 0.001	1	Se
Br	0.10 ± 0.06	<0.006	<6	0.15 ± 0.06	<0.007	<4	0.58 ± 0.04	<0.002	<0.3	Br
Rb	0.28 ± 0.06	<0.009	<3	0.15 ± 0.06	<0.009	<6	1.21 ± 0.06	0.004 ± 0.002	0.3	Rb
Sr	0.41 ± 0.08	0.025 ± 0.008	<6	<0.12	<0.012	-	0.20 ± 0.08	0.168 ± 0.008	46	Sr
Y	<0.15	<0.014	-	<0.15	<0.014	-	<0.15	0.003 ± 0.003	-	Y
Hg	<0.001	0.029 ± 0.008	~100	<0.001	0.051 ± 0.009	~100	0.025 ± 0.006	0.055 ± 0.003	69	Hg
Pb	<0.24	0.02 ± 0.01	-	<0.24	0.025 ± 0.015	-	<0.24	0.022 ± 0.004	-	Pb
K	18.8 ± 2.8	<0.24	<1	<4.11	<0.23	-	163 ± 8	0.76 ± 0.06	0.5	K
Ca	13.1 ± 1.0	13.4 ± 0.6	51	5.75 ± 0.98	0.43 ± 0.09	7	5.97 ± 1.2	8.48 ± 0.42	59	Ca
Solids		2190 ± 160			2984 ± 123			341 ± 41		Solids
	CS-64			CS-65			CS-66			
Ti	<0.57	<0.01	-	<0.60	0.068 ± 0.013	-	<0.60	0.017 ± 0.012	-	Ti
V	<0.39	0.008 ± 0.006	-	<0.42	0.020 ± 0.009	-	<0.42	0.022 ± 0.009	-	V
Cr	0.028 ± 0.005[a]	<0.007	<20	0.24 ± 0.20	0.072 ± 0.007	23	0.038 ± 0.006[a]	<0.009	<19	Cr
Mn	0.20 ± 0.14	<0.005	<2	0.22 ± 0.14	0.014 ± 0.005	6	0.27 ± 0.14	<0.007	<3	Mn
Fe	1.91 ± 0.14	0.108 ± 0.005	5	0.42 ± 0.12	1.60 ± 0.07	79	1.59 ± 0.25	0.39 ± 0.02	20	Fe
Ni	2.29 ± 0.11	0.036 ± 0.002	2	2.51 ± 0.13	0.094 ± 0.005	4	2.74 ± 1.15	0.29 ± 0.01	10	Ni
Ga	0.05 ± 0.04	<0.002	<4	0.07 ± 0.04	<0.002	<3	0.05 ± 0.04	<0.002	<4	Ga
As	3.66 ± 0.18	0.023 ± 0.001	1	2.47 ± 0.12	0.016 ± 0.001	1	14.1 ± 2.3	0.055 ± 0.003	0.4	As
Se	0.35 ± 0.04	0.003 ± 0.001	1	5.79 ± 0.29	0.045 ± 0.002	1	0.49 ± 0.08	0.007 ± 0.001	1	Se
Br	0.53 ± 0.06	<0.002	<0.4	0.61 ± 0.06	<0.002	<0.3	0.07 ± 0.06	<0.002	<3	Br
Rb	0.28 ± 0.06	<0.002	<0.7	0.34 ± 0.06	0.0047 ± 0.0020	1	0.66 ± 0.09	0.004 ± 0.002	1	Rb
Sr	<0.12	<0.003	-	0.12 ± 0.08	0.032 ± 0.003	21	0.33 ± 0.08	0.007 ± 0.003	2	Sr
Y	0.12 ± 0.10	<0.004	<3	<0.15	<0.005	-	<0.15	<0.005	-	Y
Hg	0.181 ± 0.005	0.015 ± 0.002	8	0.253 ± 0.025	0.067 ± 0.004	21	0.127 ± 0.014	0.033 ± 0.003	21	Hg
Pb	<0.24	0.006 ± 0.004	-	0.19 ± 0.18	0.006 ± 0.005	3	<0.24	0.007 ± 0.005	-	Pb
K	<4.0	<0.06	-	60.3 ± 3.1	0.33 ± 0.05	1	53.6 ± 5.1	0.23 ± 0.05	0.4	K
Ca	4.13 ± 0.92	<0.03	<1	6.2 ± 1.1	3.19 ± 0.15	34	22.9 ± 1.3	0.57 ± 0.04	2	Ca
Solids		248 ± 33			1503			337 ± 17		Solids

[a] Neutron activation analysis

Table 2. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES AND FILTERED RETORT WATERS FROM THE CONTROLLED-STATE RETORT (mg/ℓ) (cont.)

Element	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Element
	CS-67			CS-68			CS-69			
Ti	0.46 ± 0.38	<0.010	<2	0.62 ± 0.40	0.008 ± 0.007	1	0.67 ± 0.40	0.013 ± 0.010	2	Ti
V	<0.42	<0.0001	-	0.19 ± 0.07	0.017 ± 0.005	8	0.35 ± 0.28	0.018 ± 0.007	5	V
Cr	0.011 ± 0.005[a]	0.005 ± 0.003	31	0.050 ± 0.007[a]	0.004 ± 0.003	7	0.061 ± 0.006[a]	0.011 ± 0.005	15	Cr
Mn	<0.21	<0.004	<0.10	0.22 ± 0.14	<0.004	<2	<0.21	0.013 ± 0.004	-	Mn
Fe	1.07 ± 0.14	0.140 ± 0.006	12	3.22 ± 0.20	0.178 ± 0.008	5	4.35 ± 0.56	0.157 ± 0.007	3	Fe
Ni	1.26 ± 0.08	0.023 ± 0.002	2	3.61 ± 0.18	0.122 ± 0.006	3	1.52 ± 0.37	0.54 ± 0.03	26	Ni
Ga	<0.06	<0.001	-	0.07 ± 0.04	<0.001	<1	0.06 ± 0.04	<0.002	<3	Ga
As	3.50 ± 0.18	0.0105 ± 0.0008	0.3	16.9 ± 0.8	0.054 ± 0.003	0.3	7.32 ± 0.93	0.033 ± 0.002	0.5	As
Se	1.25 ± 0.06	0.0090 ± 0.0008	1	0.71 ± 0.04	0.0034 ± 0.0006	0.5	0.60 ± 0.06	0.074 ± 0.004	12	Se
Br	0.38 ± 0.04	<0.001	<0.3	0.16 ± 0.06	<0.002	<1	<0.09	<0.002	-	Br
Rb	0.29 ± 0.06	<0.002	<1	0.60 ± 0.06	0.0020 ± 0.0012	0.3	0.50 ± 0.06	0.0020 ± 0.0016	0.4	Rb
Sr	0.10 ± 0.08	<0.002	<2	0.21 ± 0.08	0.0017 ± 0.0014	1	0.21 ± 0.08	0.0035 ± 0.0022	2	Sr
Y	<0.15	0.0023 ± 0.0018	-	<0.15	<0.003	-	<0.15	<0.004	-	Y
Hg	0.090 ± 0.009	0.0099 ± 0.0016	5	0.134 ± 0.014	0.021 ± 0.002	11	0.024 ± 0.013	0.079 ± 0.004	77	Hg
Pb	<0.24	0.0028 ± 0.0026	-	<0.24	0.007 ± 0.003	-	<0.24	0.0075 ± 0.0042	-	Pb
K	4.46 ± 2.66	0.038 ± 0.029	1	43.4 ± 3.0	0.20 ± 0.03	0.5	36.7 ± 1.0	0.078 ± 0.042	0.2	K
Ca	5.76 ± 0.94	0.075 ± 0.017	1	20.0 ± 6.6	0.16 ± 0.02	1	18.8 ± 2.7	0.28 ± 0.03	1	Ca
Solids		241 ± 30			219 ± 78			375 ± 1		Solids
	CS-70			CS-71						
Ti	0.81 ± 0.40	<0.03	<4	<0.57	<0.014	-				
V	0.40 ± 0.28	0.018 ± 0.013	5	0.32 ± 0.26	0.008 ± 0.007	2				
Cr	0.055 ± 0.006	0.015 ± 0.009	21	0.043 ± 0.004[a]	<0.007	<14				
Mn	<0.21	<0.010	<0.04	<0.21	0.0076 ± 0.0036	-				
Fe	4.36 ± 0.22	0.135 ± 0.008	3	3.29 ± 0.16	0.23 ± 0.01	7				
Ni	1.52 ± 0.08	0.50 ± 0.03	25	1.94 ± 0.10	0.021 ± 0.003	1				
Ga	0.05 ± 0.04	<0.003	<6	0.05 ± 0.04	<0.002	<4				
As	7.48 ± 0.37	0.059 ± 0.023	1	4.57 ± 0.23	0.025 ± 0.003	1				
Se	0.57 ± 0.04	0.101 ± 0.006	15	0.33 ± 0.04	0.0017 ± 0.0010	1				
Br	<0.09	<0.004	-	0.14 ± 0.04	<0.002	<1				
Rb	0.50 ± 0.06	0.0069 ± 0.0031	1	0.17 ± 0.06	<0.002	<1				
Sr	0.21 ± 0.08	0.0077 ± 0.0040	4	0.21 ± 0.08	0.0083 ± 0.0022	4				
Y	<0.15	0.0068 ± 0.0048	-	<0.15	<0.004	-				
Hg	0.025 ± 0.007	0.073 ± 0.005	74	0.048 ± 0.002	0.0019 ± 0.0003	4				
Pb	<0.24	0.011 ± 0.008	-	<0.21	<0.006	-				
K	36.1 ± 2.9	0.24 ± 0.09	1	18.7 ± 2.7	0.077 ± 0.043	0.4				
Ca	23.8 ± 1.2	0.34 ± 0.05	1	14.0 ± 1.0	0.93 ± 0.10	6				
Solids		451 ± 32			203 ± 46	Solids				

[a] Neutron activation analysis

bromine, and rubidium. The percent particulate is significantly greater than 1% for iron, chromium, mercury, and nickel in most samples.

Three of the filtered samples (CS-66, -68 and -69) exhibited remarkable visual changes during storage at room temperature. All three samples became turbid and a finely divided deposit collected at the bottom of each container. Similar, but less marked behavior was noted in all filtrates left at room temperature. No visual changes occurred in the samples stored at <4° C. These three samples were filtered after 15 to 17 days of storage at room temperature and the particulates analyzed. The elemental composition of particulates collected from these three waters during the first and second filtration are compared in Table 3. This table shows that there is a significant concentration of solids and of all of the elements in the particulate fraction from the second filtration. The ratio of the solids from the second to those from the first filtration is 0.69 ± 0.08, i.e., 69% of the mass collected during the first filtration was again collected during the second. This could only occur if the first filtration was not successful in removing all the particulates that can be captured by a 0.45 μm filter (not likely) or if significant bacterial activity occurred in the sample. The visual appearance of the samples (sediment at the bottom of the container) plus the work of Farrier[1] support the conclusion that the high solids level obtained on the second filtration is largely due to bacterial growth. Microscopic examination of the sediment from one of the waters revealed rod-shaped structures similar to those reported by Farrier.[1]

The effect of this sediment on the concentration of nine elements was examined by sampling the top and bottom 1 mm of three waters that had been stored under ambient conditions for about 1 year. The results of these determinations, shown in Table 4, indicate that there is a concentration gradient between the top and bottom of the sample container for mercury, nickel, arsenic, iron, germanium, bromine, and selenium. The majority of the mercury and varying amounts of the other elements is at the bottom of the container in the sediment. This suggests that the bacterial cells remove these elements from solution. The high percent particulate values for mercury and nickel in Table 2 support this.

The uniformly high level of most of the elements measured in the particulates from the second filtration (Table 3) cannot be entirely explained by removal by bacteria. As will be seen in discussion to follow, precipitation during filtration is an important factor.

Particle Morphology

The morphology and chemical composition of individual particles present in the particulate fraction of each water are presented in Figs. 1-12. This series of figures presents scanning electron micrographs of particulates from each water and x-ray spectra of individual particles shown in the micrographs. Since only a small area is represented by each micrograph, it should not be assumed that the types of particles present are limited to those shown.

A visual classification of the particles reveals that there are two types present: crystals and amorphous solids. These particles are imbedded

Table 3. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES FROM FIRST AND SECOND FILTRATION OF WATERS CS-66, CS-68 AND CS-69 (ng/ml)

Element	CS-66		CS-68		CS-69	
	First Filtration	Second Filtration[a]	First Filtration	Second Filtration[a]	First Filtration	Second Filtration[a]
As	54.6 ± 2.7	80.2 ± 4.0	54.1 ± 2.7	84 ± 4	33.1 ± 1.7	81.6 ± 4.0
Br	<2.4	<3.3	<1.5	<2.4	<2.4	<4.5
Ca	573 ± 35	334 ± 34	156 ± 17	<43	282 ± 26	2990 ± 150
Cr	<8.7	9.9 ± 6.0	4.1 ± 3.2	<8.4	10.9 ± 4.8	14.6 ± 11.6
Cu	5.2 ± 3.0	29.1 ± 4.0	41.4 ± 2.1	230 ± 11	63.4 ± 3.4	<13.5
Fe	390 ± 18	202 ± 10	178 ± 8	168 ± 8	157 ± 7	83.5 ± 43
Ga	<2.1	<2.1	<1.2	<2.1	<1.8	<3.9
Hg	33.2 ± 3.4	142 ± 7	20.9 ± 1.8	11.2 ± 2.8	78.6 ± 3.9	14.3 ± 6.0
K	228 ± 54	374 ± 55	201 ± 30	276 ± 52	78.3 ± 42.2	291 ± 106
Mn	<6.9	<6.9	<3.6	<6.6	12.8 ± 4.0	12.7 ± 9.0
Ni	294 ± 14	977 ± 48	122 ± 6	195 ± 9	542 ± 27	225 ± 11
Pb	6.8 ± 4.8	<7.5	6.7 ± 2.6	<7.5	7.5 ± 4.2	<14.7
Rb	4.0 ± 2.0	4.1 ± 2.0	2.0 ± 1.2	2.5 ± 2.0	2.0 ± 1.6	6.1 ± 4.0
Se	6.5 ± 1.2	32.7 ± 1.6	3.4 ± 0.6	5.3 ± 1.2	73.7 ± 3.7	19.7 ± 2.6
Sr	6.5 ± 2.6	6.8 ± 2.6	1.7 ± 1.4	<3.9	3.5 ± 2.2	29.0 ± 5.4
Ti	17 ± 12	<18	7.6 ± 6.6	<18	13.3 ± 9.8	<35.1
V	22 ± 9	<13	17.0 ± 4.8	9.6 ± 8.6	18.0 ± 7.2	<25.2
Y	<4.8	<4.8	<2.7	<4.5	<3.9	<9.3
Zn	68.6 ± 3.4	13.0 ± 2.2	114 ± 5	133 ± 6	156 ± 7	9.6 ± 4.8
Total Solids	337 ± 17	257 ± 16	219 ± 78	153	375 ± 1	228 ± 1

[a]The second filtration was performed on the filtrate from the first filtration after it had been maintained at room temperature for 15 to 17 days.

Table 4. X-RAY FLUORESCENCE ANALYSES OF THE TOP AND BOTTOM 1 mm OF LIQUID IN WATERS CS-64, CS-65 AND CS-67 AFTER STORAGE FOR 1 YEAR AT ROOM TEMPERATURE (ng/ml)

	CS-64		CS-65		CS-67	
Element	TOP	BOTTOM	TOP	BOTTOM	TOP	BOTTOM
As	4.6 ± 0.2	5.5 ± 0.2	3.1 ± 0.2	4.9 ± 0.2	5.4 ± 0.2	4.3 ± 0.2
Br	0.4 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	1.2 ± 0.2	0.5 ± 0.1	0.5 ± 0.1
Fe	1.1 ± 0.4	2.5 ± 0.4	<0.5	0.7 ± 0.4	1.0 ± 0.4	1.6 ± 0.4
Ge	<0.2	0.3 ± 0.1	<0.2	0.4 ± 0.1	<0.2	0.3 ± 0.1
Hg	0.072 ± 0.011	0.75 ± 0.014	0.059 ± 0.005	0.78 ± 0.08	0.065 ± 0.008	0.51 ± 0.10
Ni	2.2 ± 0.2	4.9 ± 0.3	2.0 ± 0.2	5.5 ± 0.3	1.3 ± 0.2	3.2 ± 0.3
Rb	0.3 ± 0.2	0.3 ± 0.2	0.4 ± 0.2	0.6 ± 0.2	0.3 ± 0.2	0.4 ± 0.2
Se	0.4 ± 0.1	0.5 ± 0.1	4.5 ± 0.2	12.3 ± 0.4	2.0 ± 0.2	1.8 ± 0.1
Sr	<0.3	<0.3	0.3 ± 0.2	0.3 ± 0.2	0.2 ± 0.2	<0.3

in a uniform background of spongy or scaly material. The only element detected in the matte material is sulfur (carbon and nitrogen are likely to be present but cannot be detected by EDAX). The amorphous particles are rounded (see Figs. 4 and 5) and their chemical composition is silicon-aluminum-(calcium, potassium, iron, sodium). The crystalline particles are varied in shape and are composed of iron, calcium, magnesium or nickel. The particles range in size from a micron or less to about 100 μm.

The rounded amorphous particles are hypothesized to be spent shale particles. This is supported by their composition and their similarity to individual particles of spent shale and is consistent with the mineral composition of spent shale particles.[5]

The crystalline particles are highly varied in both form and chemical composition. Three rather striking crystal types were obtained. Filtration of water CS-62 (from an inert gas run using Utah shale) produce a high density of cubic crystals (3 μm sides) of iron and nickel (see Fig. 2). The associated anion is unknown. The small size of the crystals prevented their identification by x-ray diffraction techniques. The unique formation of nickel-iron crystals during filtration of water CS-62 is consistent with the chemical composition of unfiltered water. This water contains 10.7 mg/l of nickel, 15.3 mg/l of iron and 2.8% sulfur. These are the highest values of these three elements found in any of the 11 waters.

Filtration of water CS-63 (from an inert gas run using Antrim shale) produced a high density of long needle-like crystals in a radial array with a daimeter of about 7 μm (Fig. 3). The simultaneous presence of high levels of strontium, magnesium, potassium and sulfur distinguish this water from others in the set studied. EDAX analyses indicate that the only cation present is calcium. X-ray diffraction on individual crystals identified the mineral phase as aragonite. Solubility calculations support the x-ray diffraction identification. Water CS-63 is supersaturated with respect to both aragonite and calcite. The crystallization of aragonite is favored by the presence of small amounts of barium, strontium, magnesium or lead salts and $CaSO_4$, by rapid precipitation and by relatively high concentrations of reactants.[6] All of these conditions are met for water CS-63.

Water CS-69 (from a steam combustion run using Colorado shale) produced a high density of prismoidal crystals (30 μm side) in which the predominant cation is magnesium (Fig. 9). These larger crystals coexist with clusters of microcrystals of magnesium and sulfur. The larger crystals are probably magnesium carbonate and the microcrystals are probably gypsum ($CaSO_4 \cdot 2H_2O$). Solubility calculations indicate water CS-69 is supersaturated with respect to magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$) and hydromagnesite ($Mg_4(CO_3)_3(OH_2) \cdot 3H_2O$). Other work[6] indicates that precipitation at ordinary temperature and pressure gives either nesquehonite or a basic carbonate such as hydromagnesite. Thus, the larger crystals are likely one of these forms of magnesium carbonate. X-ray diffraction on individual crystals failed to identify the mineral phase. The crystals apparently decomposed between the initial filtration and the x-ray diffraction work (∿ one year). This was verified by re-examining the deposits by scanning electron microscope. The crystals present in CS-69 had been replaced by deposits similar to those shown in the micrographs in Figs. 1

and 10 suggesting that both of these deposits may have contained crystalline material at one time.

A number of other particles with a predominance of a single cation, either calcium, magnesium, iron, aluminum or silicon, was also identified. The density of these other particles was lower and their structure was not readily discernible from the data at hand. Examples of these other particles include: (1) concave particles with dark centers in which iron is the predominant cation (particle 2A in Fig. 3 and particle 2D in Fig. 7), (2) rounded amorphous particles in which silicon, likely as SiO_2, is the predominant cation (all particles in Fig. 5, and particle 1A in Fig. 6), and (3) obscured particles in which aluminum is the predominant cation (particle 3A in Fig. 10 and particle 1C in Fig. 9).

Other particles were observed in which no element, except sulfur, was found (indicating a composition of elements lighter than aluminum). The sulfur, in all cases, is attributed to the background matte and not the particle. Examples of these crystals are seen in Fig. 2 (particles 1A, 2A, 1C-4C) and Fig. 6 (particles 4A, 5A). Based on the composition of retort waters, these particles may be such compounds as NH_4HCO_3, $NH_4(CO_3)_2$ or salts of organic acids, such as $(NH_4)_2C_2O_4 \cdot H_2O$.

Particle Formation Mechanisms

Four mechanisms are adequate to explain the origin and composition of retort water particulates. These four mechanisms are: (1) oil and spent shale particle suspension during retorting, (2) evaporation of an equivalent 1 mm deep layer of retort water from the filter surface, (3) crystal formation during filtration due to CO_2 outgassing and (4) bacterial removal. These mechanisms explain the following major observations:

(1) The particulate fraction consists of a uniform fibrous matte in which individual crystalline or amorphous particles are embedded.

(2) The concentration of 19 elements and solids in particulates collected during two successive filtrations of the same water are similar.

(3) The elements calcium, magnesium, iron, silicon, aluminum, potassium, sodium, nickel, barium, and chromium are localized in individual particles and are the major elements in the particulates. The elements arsenic, selenium, rubidium, strontium, mercury, gallium, lead, yttrium, titanium, and manganese are uniformly distributed in the matte material and occur at low levels, typically less than 10 μg/l.

(4) One percent or less of the total mass of potassium, arsenic, selenium, bromine, and rubidium and considerably more than 1% of the iron, nickel, mercury, and chromium present in the unfiltered water occur in the particulate fraction.

(5) A significant concentration gradient may exist between the top and bottom of an unrefrigerated sample for the elements mercury, nickel, germanium, arsenic, bromine, iron, and selenium.

(6) The elemental composition and morphology of the amorphous particles are similar to spent shale. Crystalline particles are typically composed of either calcium, magnesium or iron.

Suspension of Spent Shale Fines and Oil—

Oil shale becomes friable during retorting due to the removal of kerogen from the mineral matrix. Bed settling and errosion by hot combustion gases may release spent shale fines which are entrained in the gases and either settle out or are entrapped during the condensation of oil and water vapors. Spent shale fines are composed of akermanite, diopside, calcite, albite, analcime and other minerals; the principal elements are silicon, aluminum, calcium, iron, magnesium, and sodium.[5] The morphology and composition of these fines are very similar to the silicon-aluminum-(calcium, magnesium, iron, sodium) particles that are present in most of the waters. The round shape of these particles, suggesting heat treatment, also supports the theory that they are spent shale fines.

Oil and water condense out of the gas phase and move down the packed bed as an emulsion. After separation of these phases, a small amount of oil remains in the water phase. This oily material is removed during filtration of the sample and collects as a spongy fibrous matte on the filter paper. This is supported by its visual appearance, texture and odor and by the presence of a strong sulfur peak in the x-ray spectrum of the backgrounds of most of the samples. Calculations indicate that this oil does not significantly contribute to the measured elemental abundances in retort water particulates (<1%).

Surface Evaporation—

Since the organic matte (oil and bacterial cells) and filter paper are hygroscopic, some of the filtered water is retained following filtration. When this retained water is evaporated, the dissolved ions present in it are deposited on the filter paper. If it is assumed that the equivalent moisture film thickness is 1 mm, then about 0.14 ml of water is retained on the filter paper for a deposit with a diameter of 42 mm. If 25 ml of sample are filtered, then 0.55% of the total elemental mass in the unfiltered sample will be deposited approximately uniformly. This is within an order of magnitude of the amount of potassium, arsenic, selenium, bromine, rubidium and titanium found in all of the particulates for which 25 ml were filtered. Five ml of waters CS-60 and CS-62 and 10 ml of water CS-69 were filtered. Thus, about 1.5% and 3% of the elemental mass in the unfiltered sample should be deposited for the 10 ml and 5 ml samples, respectively. This is consistent within an order of magnitude (see Table 2) with the particulate data and the elemental abundance data for potassium, arsenic, selenium, bromine, and rubidium.

Surface evaporation of a 1 mm layer is also supported by the fact that the particulate composition in two successive filtrations is similar and by the fact that the elements occurring at low levels in the particulates (i.e., about the right order of magnitude to have been deposited by evaporation of a 1 mm layer) are not localized in the particulates with the exception of potassium (occurs in spent shale fines).

Precipitation —

The crystals noted in some particulates probably form during filtration. If these crystals were formed during or immediately subsequent to retorting, they would likely redissolve as the solubility of carbonates decreases at elevated temperatures.

Most retort waters are supersaturated with respect to a number of mineral phases such as calcite, aragonite, magnesite and siderite. However, the high concentration of organics in these waters may increase the solubility relative to that predicted for infinitely dilute solutions. During filtration, CO_2 is stripped out of solution. This drives the reaction

$$MeCO_3(s) + CO_2(g) + H_2O \rightleftharpoons Me^{+2} + 2HCO_3^-$$

to the left and metal carbonates ($MeCO_3$) may precipitate.

This is dramatically supported by the presence of calcium and magnesium carbonates in the particulates. It is also supported by the high percent particulates for iron, nickel, calcium, magnesium and chromium in Table 2 and by the localization of these elements in particles. The very high percent particulates and high elemental masses for iron, nickel and calcium relative to other elements can only be explained by the precipitation of carbonates of these elements during filtration. About half or more of the iron, nickel and calcium were removed, presumably as crystals, during the filtration of waters CS-60, -62 and -63. Surface evaporation, presence in the oil fraction or bacterial removal cannot explain the high values. Crystals were not observed in water CS-60, presumably due to crystal decomposition prior to analysis as was verified for water CS-69.

Bacterial Removal

Bacterial cells that accumulate at the bottom of a sample container stored at $>4^\circ$ C may remove a significant fraction of the dissolved mercury, nickel and selenium and lesser amounts (<5%) of arsenic, bromine and iron. High concentrations of rod-shaped bacteria have been identified in the sediment that accumulates in retort waters stored at room temperature.[1] These bacteria have a surface charge and provide a high specific surface area which enhances adsorption. They may also remove elements by biological uptake. Table 4 indicates that large amounts of mercury and nickel are associated with the sediment material in all three samples studied and that lesser amounts of arsenic, bromine, iron, germanium and selenium are associated with the sediment of one or more of the samples. The most dramatic example of this behavior occurs for mercury. The samples in Table 2 with a high percent particulate loading for mercury (CS-60, -62, -63, -69, and -70) also have elevated percent particulate values for chromium, selenium and nickel relative to samples with low percent mercury particulate values. These elevated values cannot be explained by any of the previously discussed mechanisms and are likely due to association with the sediment material.

SUMMARY

Particulates were collected from 11 retort waters and their chemical composition and morphology studied using x-ray fluorescence spectrometry, x-ray diffraction and scanning electron microscopy. This work indicates that the particulate fraction of retort water consists of oils and tars, spent shale fines and bacterial cells. Crystals and finely dispersed salts may form during or after vacuum filtration and contribute to the particulate fraction. The crystal phase aragonite was positively identified in one sample. These particulates originate from the suspension of spent shale fines and the formation of an oil-water emulsion during retorting, from the evaporation of an equivalent 1-mm-deep layer of retort water from the filter surface, from CO_2 outgassing during filtration and from bacterial growth in samples maintained at >4° C.

The elements calcium, magnesium, iron, silicon, aluminum, potassium, sodium, nickel, barium, and chromium may be localized in individual particles and are major elements in the particulates. About one percent of the total potassium, arsenic, selenium, bromine, and rubidium in retort water is present in the particulate fraction and significantly greater than one percent of the iron, chromium, mercury and nickel. The elements arsenic, selenium, rubidium, strontium, mercury, gallium, lead, yttrium, titanium, and manganese are uniformly distributed in the matte material and occur at low levels. The elements mercury, nickel, germanium, arsenic, bromine, iron, and selenium appear to be removed by the bacterial cells.

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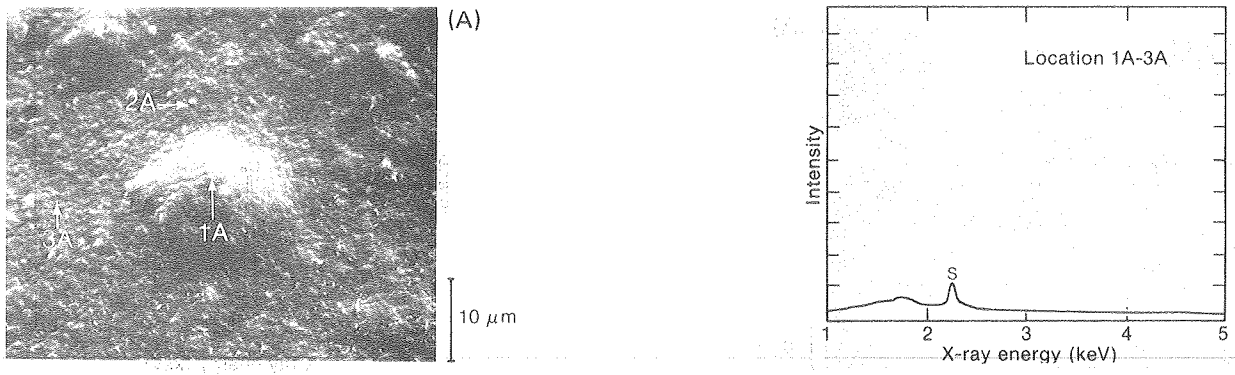

Figure 1. Scanning electron micrograph of (A) particulates from water CS-60 and diagrams of x-ray energy at locations 1A-3A. XBB 788-10560

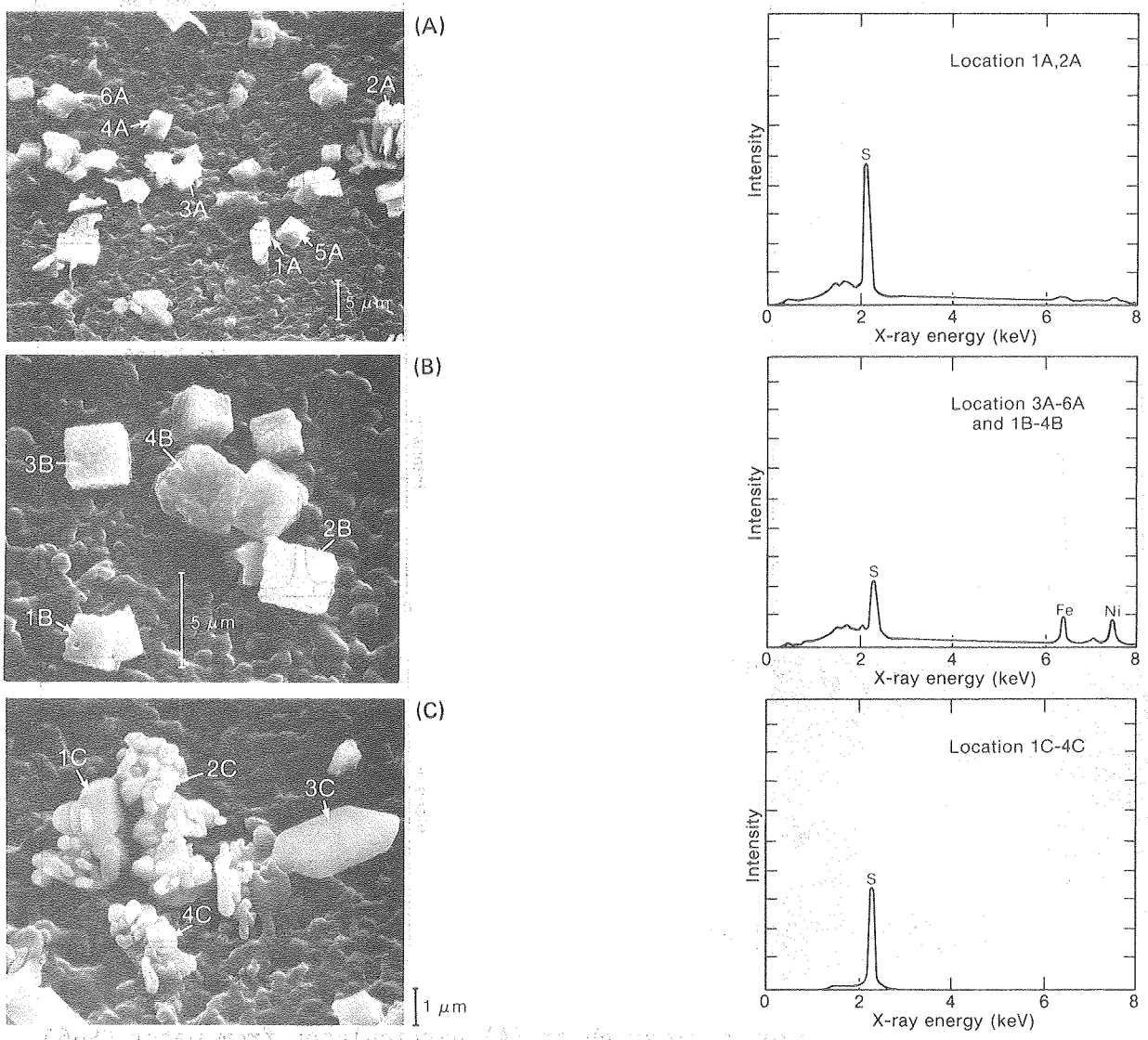

Figure 2. Scanning electron micrograph of (A) particulates from water CS-62; (B) particulates similar to those at locations 4A-6A in (A); (C) particulates from water CS-62; and diagrams of x-ray energy at locations 1A, 2A; 3A-6A and 1B-4B; and 1C-4C.

XBB 788-10557, 58 and 59

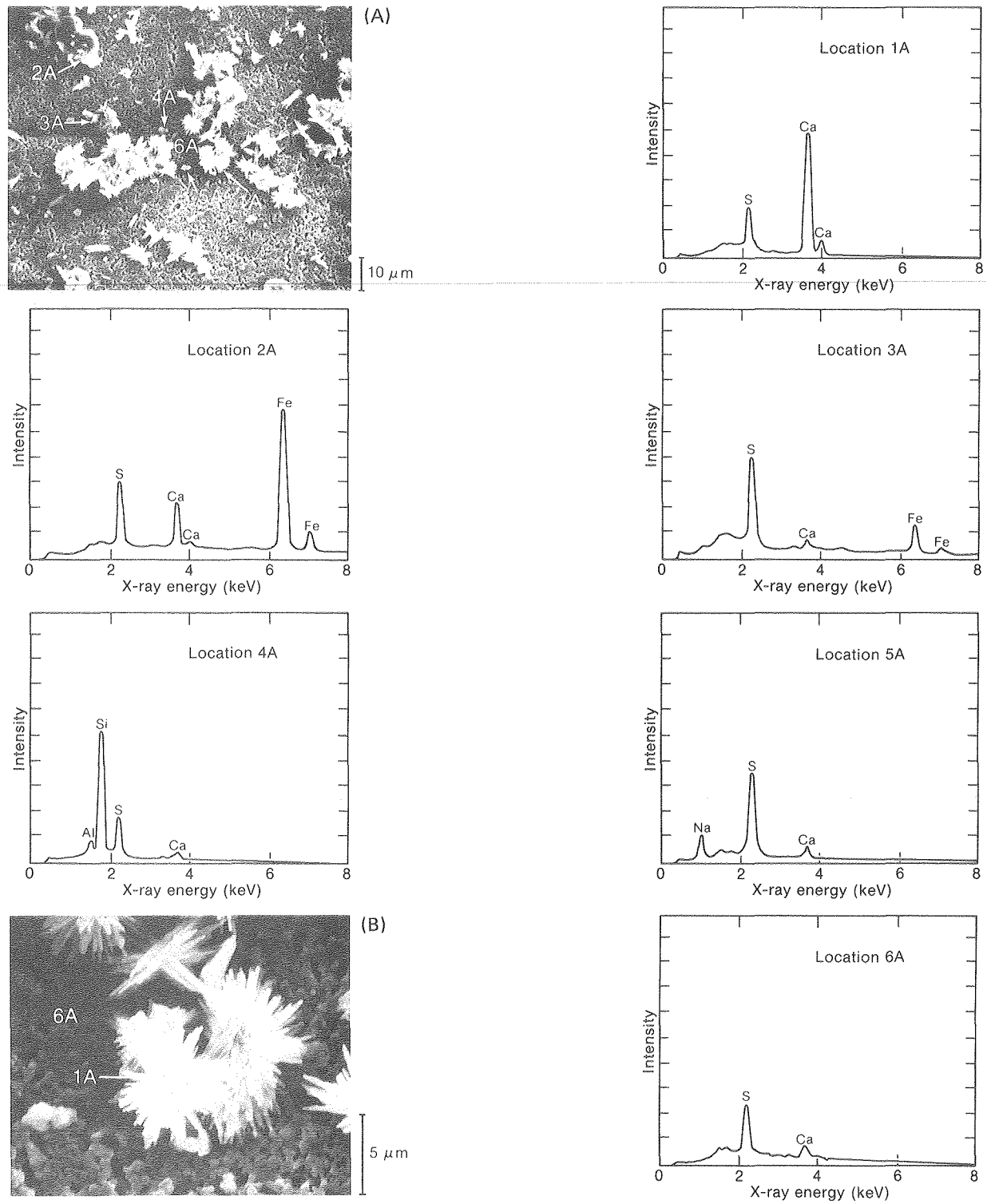

Figure 3. Scanning electron micrograph of (A) particulates from water CS-63; (B) detail of location 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; 4A; 5A; and 6A. XBB 788-10567 and 69

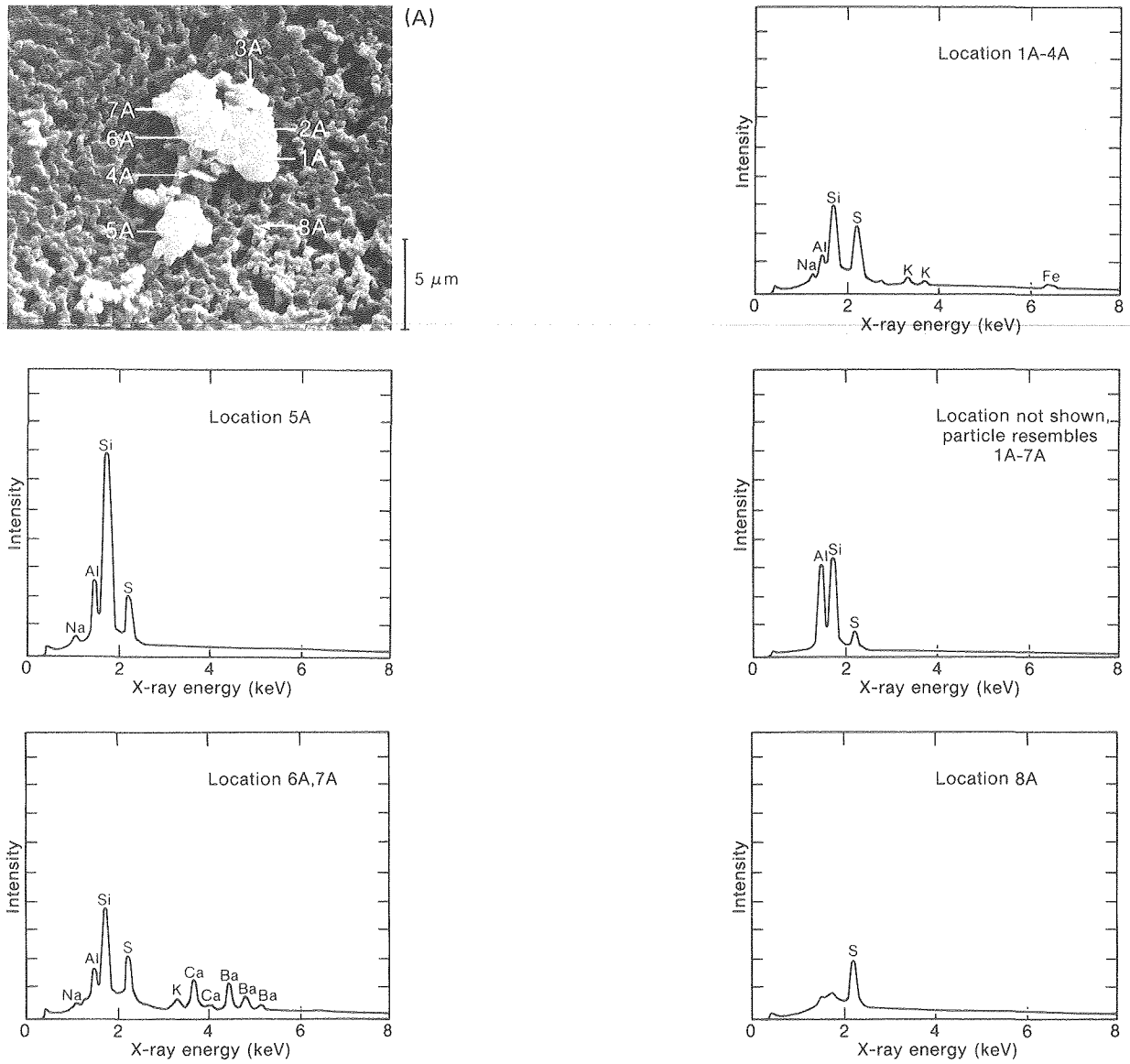

Figure 4. Scanning electron micrograph of (A) particulates from water CS-64; and diagrams of x-ray energy at locations 1A-4A; 5A; location resembling 1A-7A; 6A and 7A; and 8A. XBB 788-10568

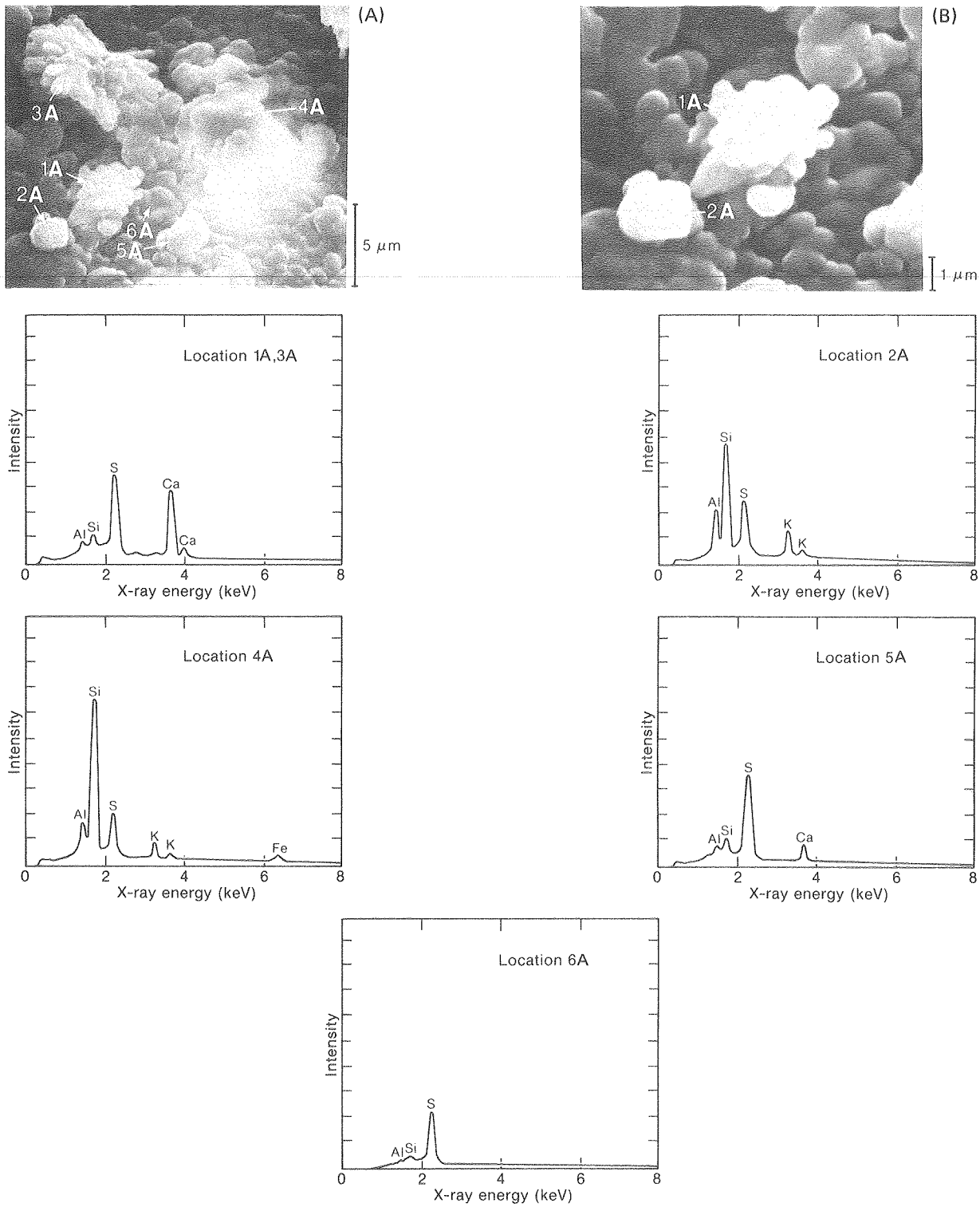

Figure 5. Scanning electron micrograph of (A) particulates from water CS-65; (B) detail of locations 1A,2A; and diagrams of x-ray energy at locations 1A, 3A; 2A; 4A; 5A; and 6A XBB 788-10572 and 74

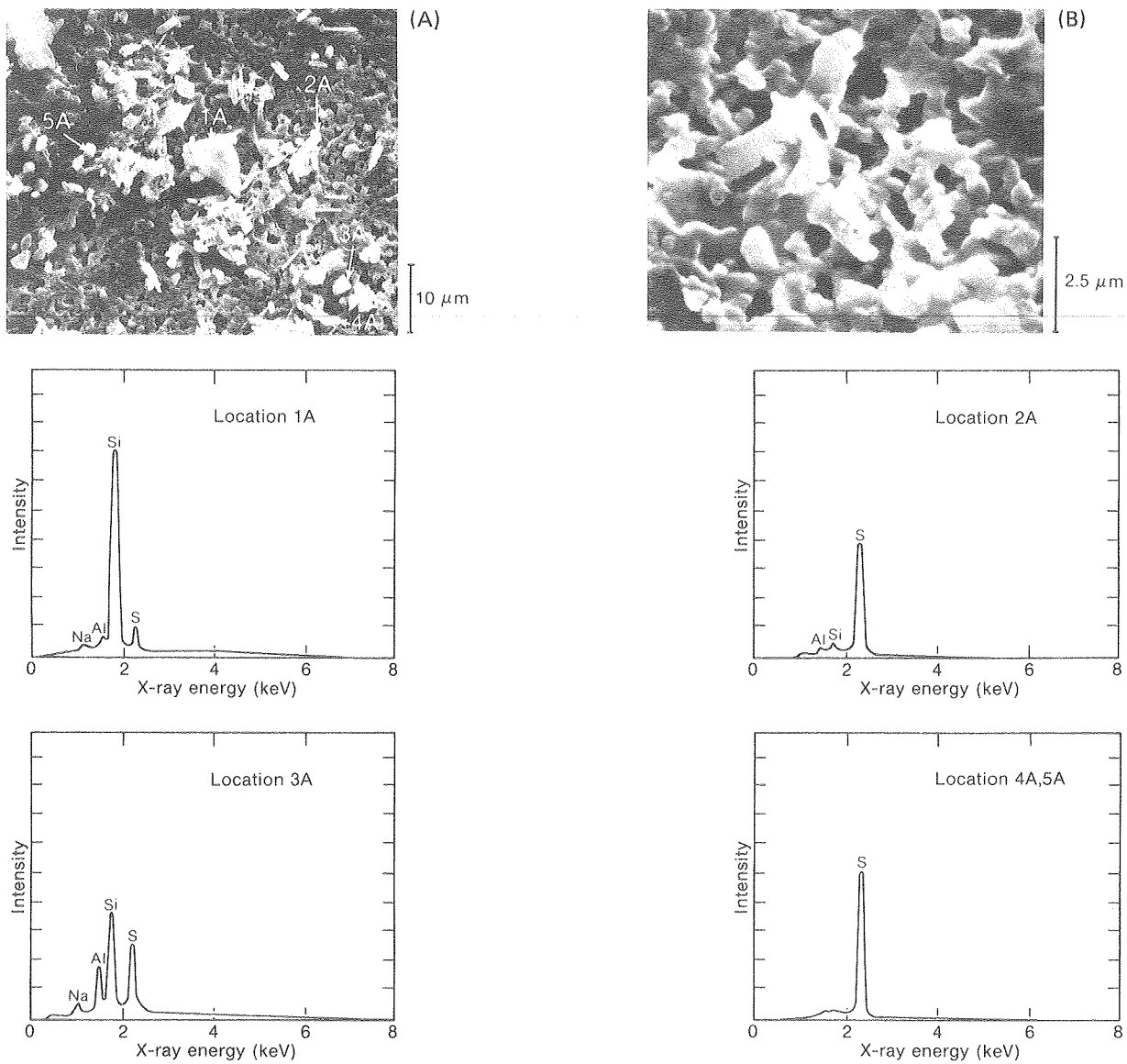

Figure 6. Scanning electron micrograph of (A) particulates from water CS-66; (B) detail of background in vicinity of location 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; and 4A, 5A.

XBB 788-10578 and 80

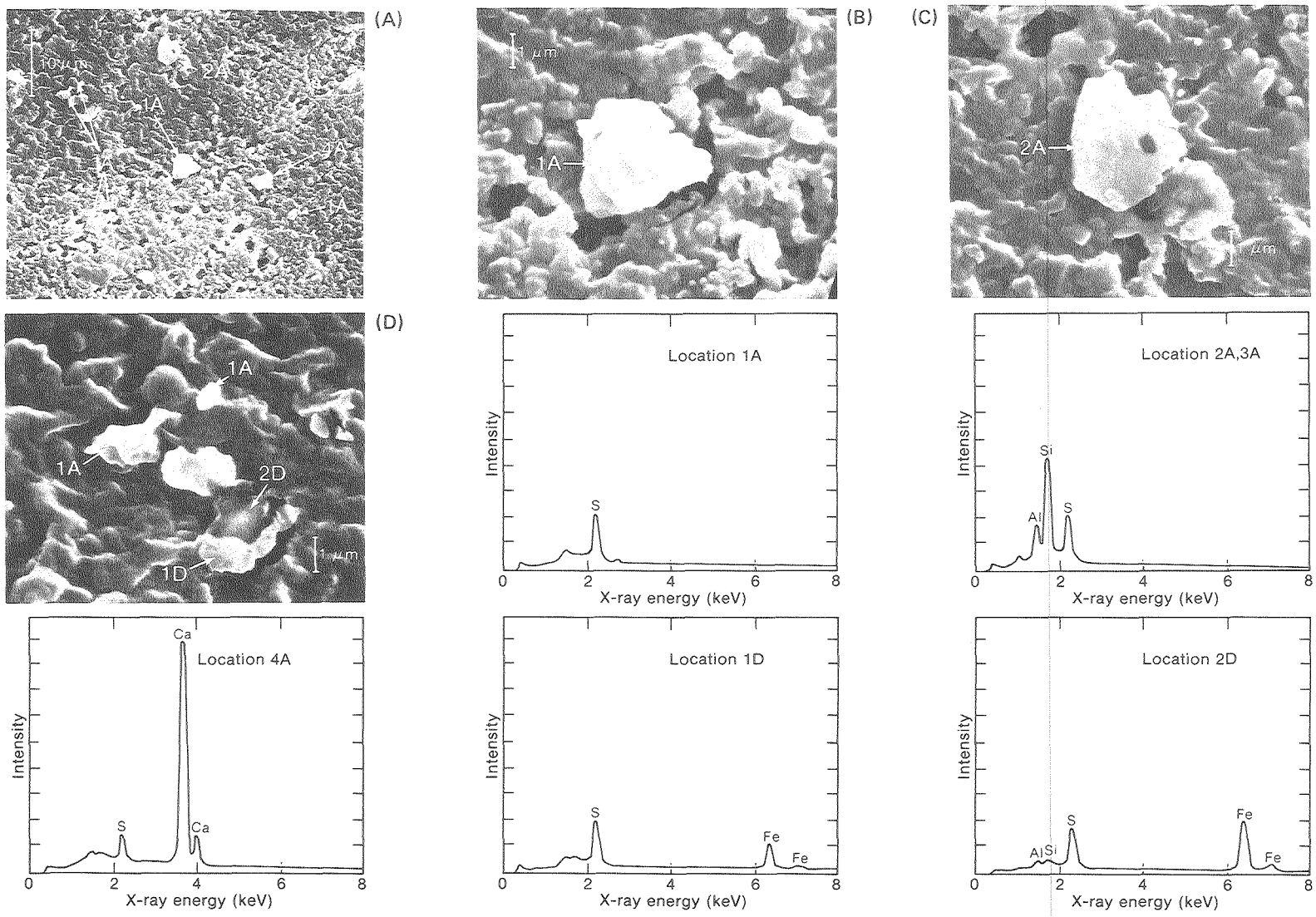

Figure 7. Scanning electron micrograph of (A) particulates from water CS-67; (B) detail of 1A at center field; (C) detail of 2A at top centers; (D) detail of upper left field; and diagrams of x-ray energy at locations 1A; 2A, 3A; 4A; 1D; and 2D.

XBB 788-10579, 76, 77, and 75

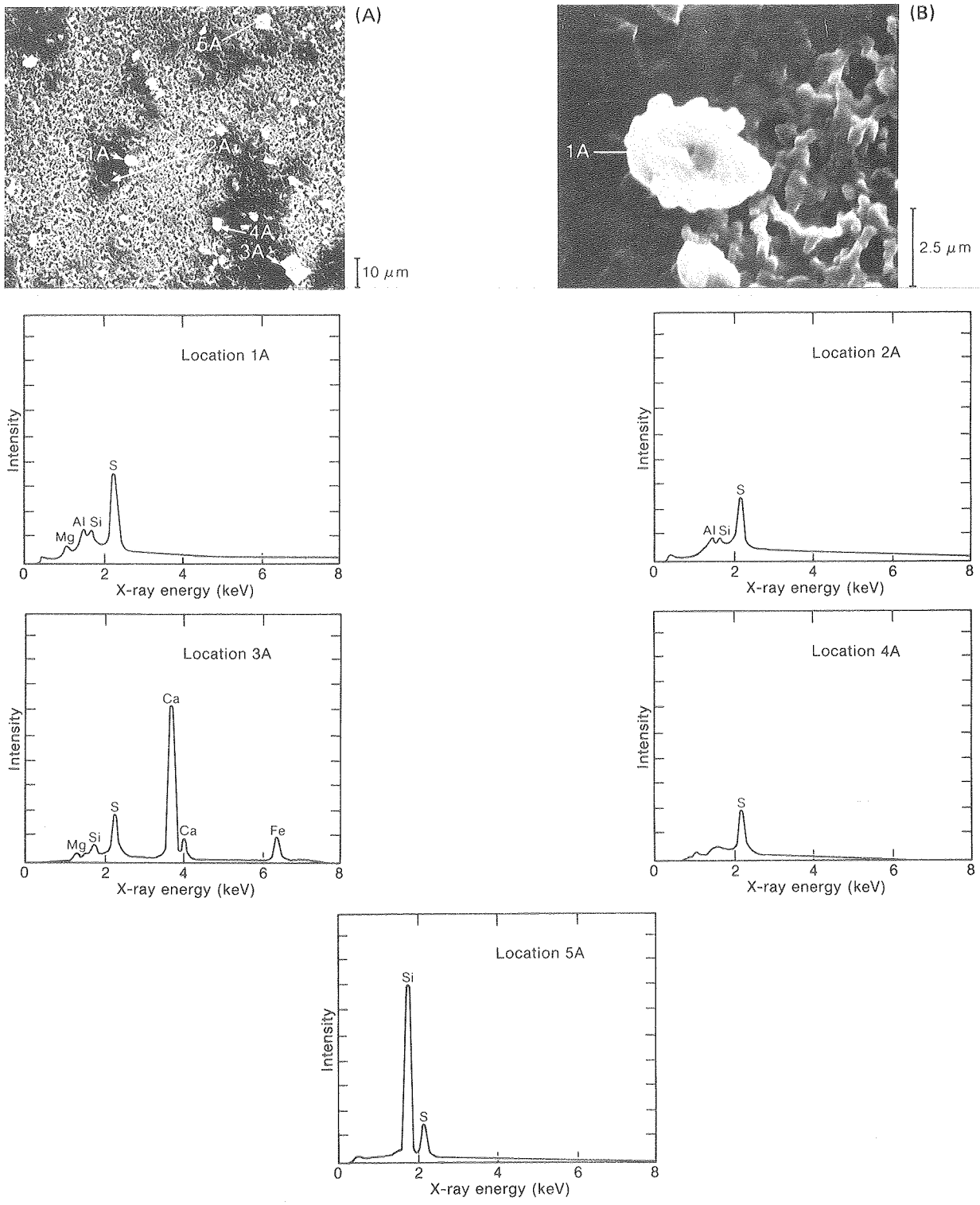

Figure 8. Scanning electron micrograph of (A) particulates from water CS-68; (B) detail of 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; 4A; 5A XBB 788-10571 and 70

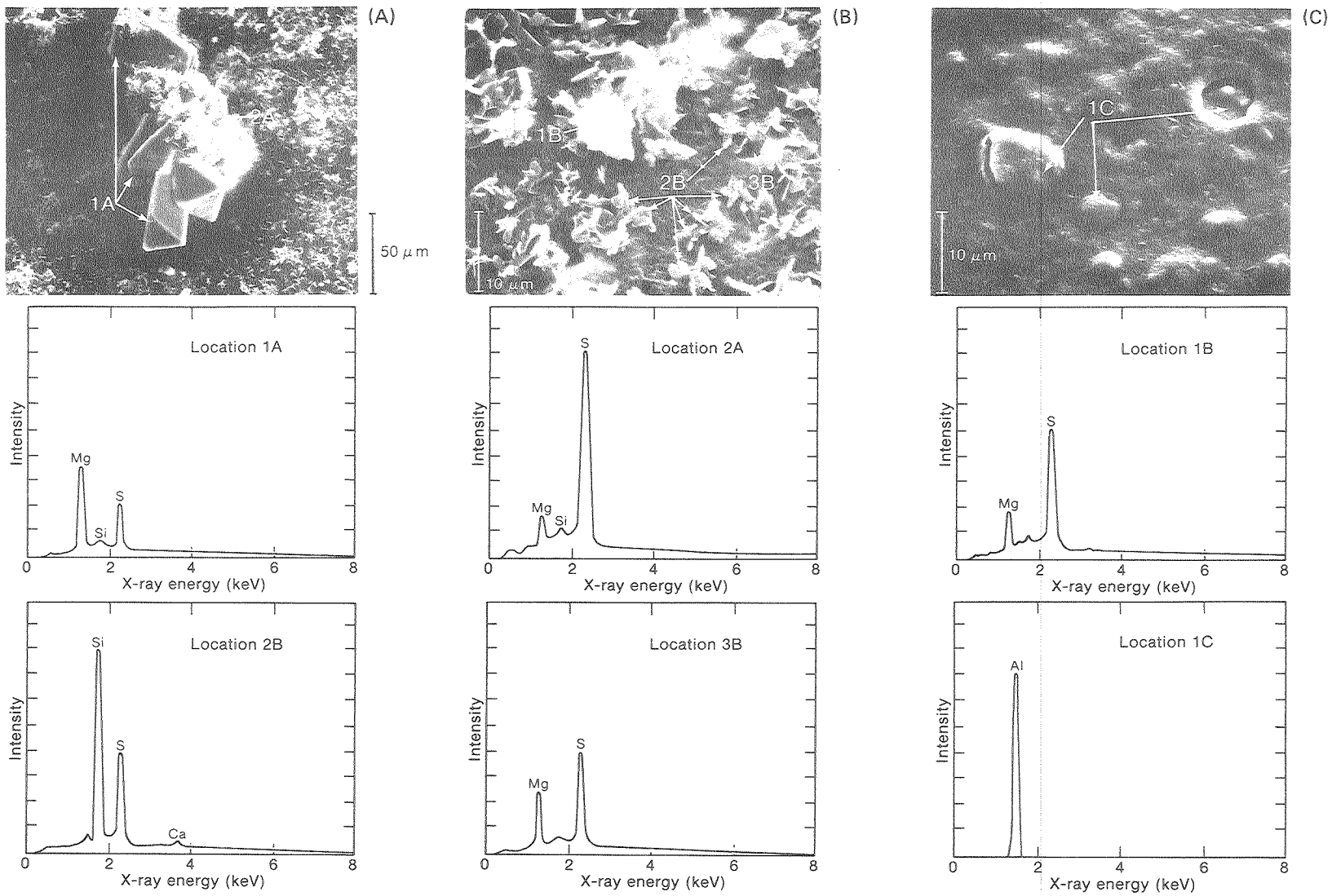

Figure 9. Scanning electron micrograph of (A) particulates from water CS-69; (B) more particulates from water CS-69; (C) particulates from water CS-69 one year after micrographs (A) and (B); and diagrams of x-ray energy at locations 1A; 2A; 1B, 2B; 3B; and 1C.
XBB 788-10565, 66 and XBB 795-6531

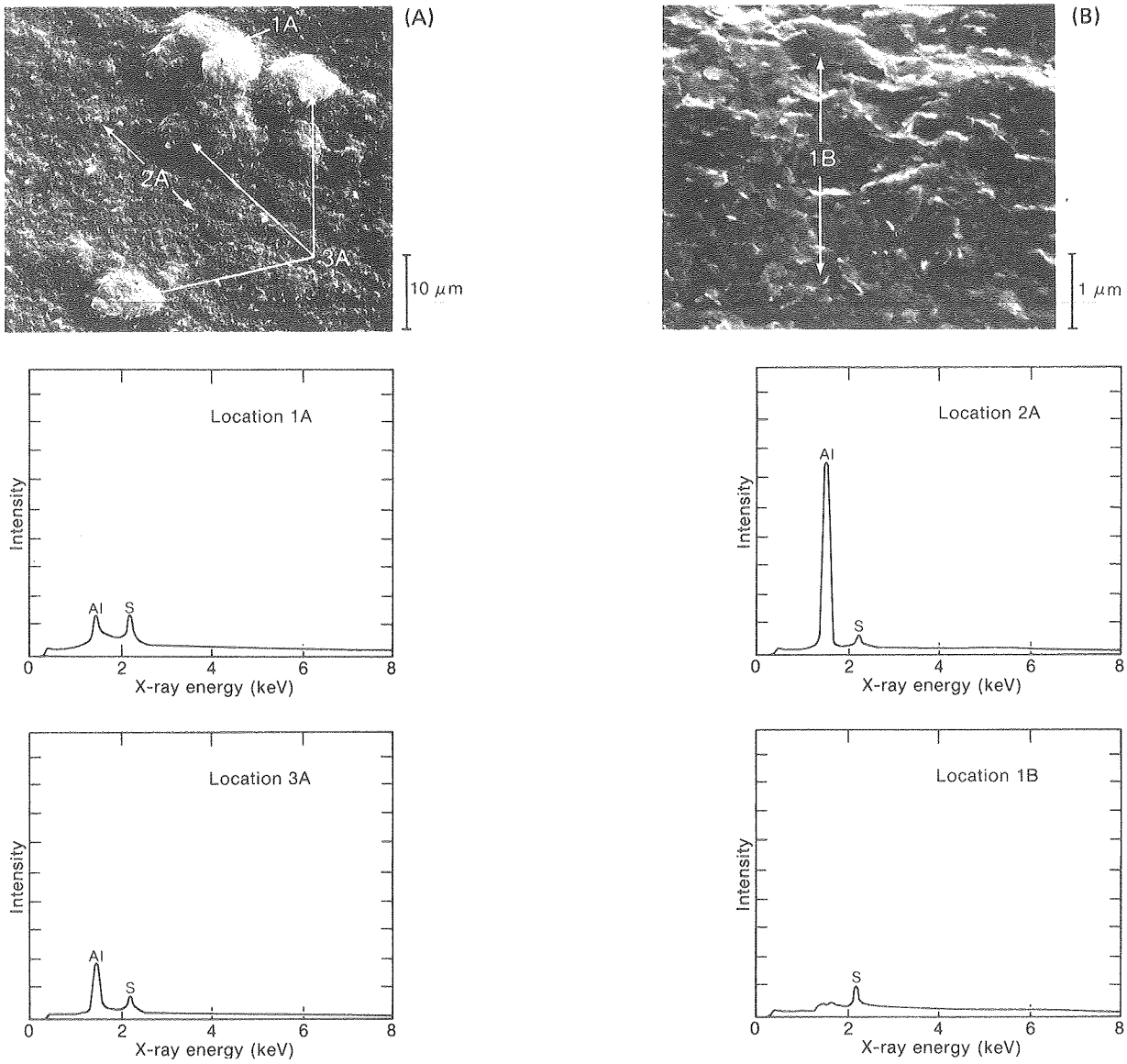

Figure 10. Scanning electron micrograph of (A) particulates from water CS-70; (B) more particulates from water CS-70; and diagrams of x-ray energy at locations 1A; 2A; 3A; and 1B. XBB 788-10563 and 62

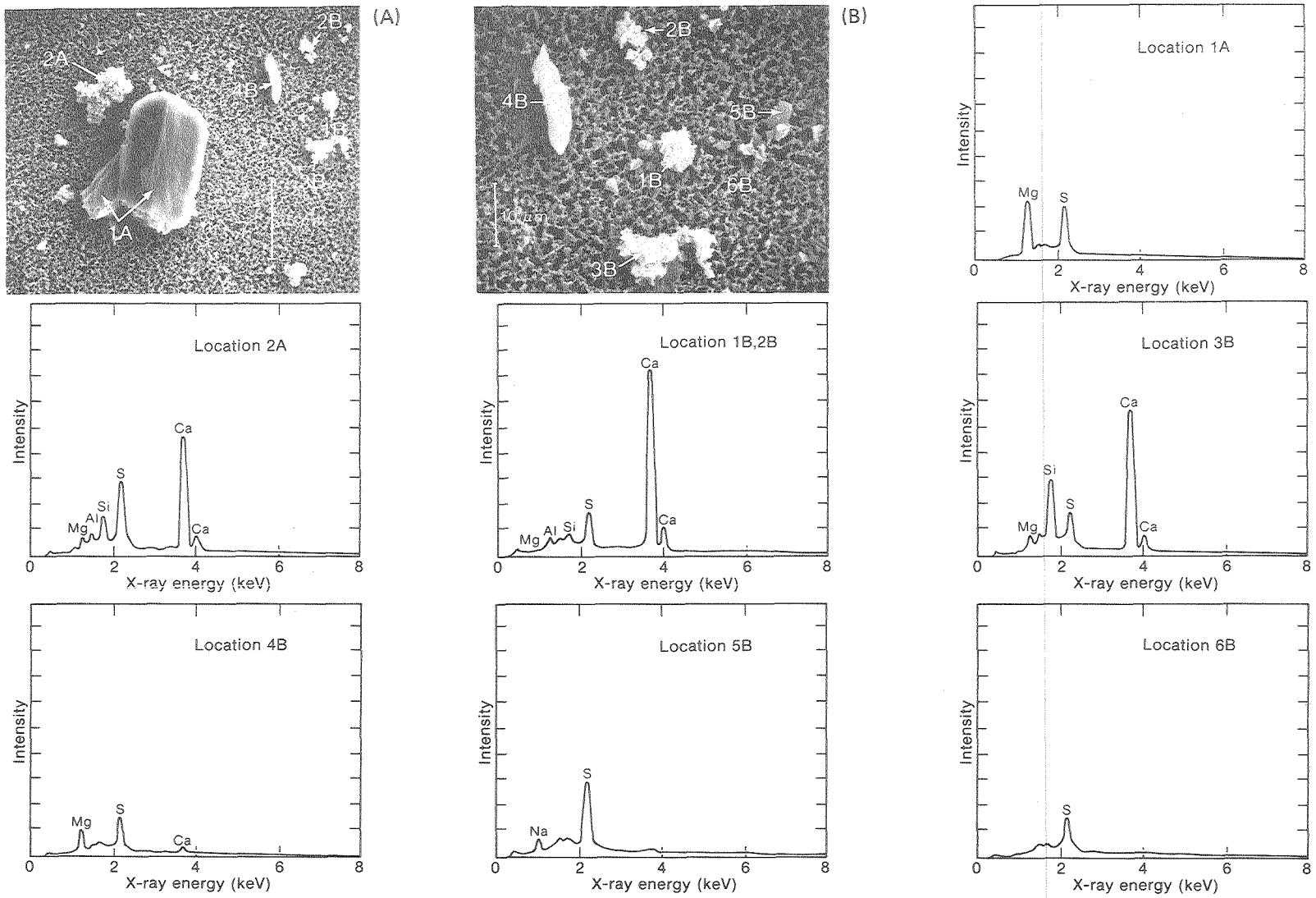

Figure 11. Scanning electron micrograph of (A) particulates from water CS-71; (B) detail of upper right field of (A); and diagrams of x-ray energy at locations 1A; 2A; 1B, 2B; 3B; 4B; 5B; and 6B. XBB 788-10555 and 56

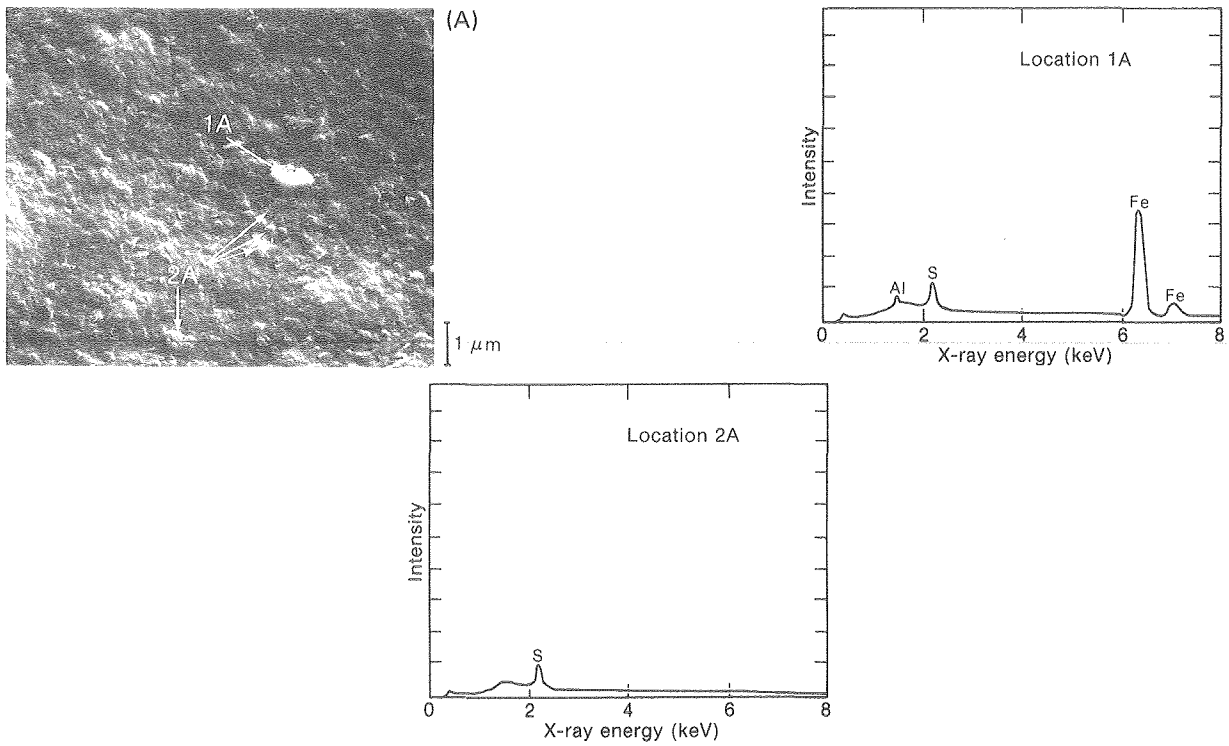

Figure 12. Scanning electron micrograph of (A) particulates from refiltered water CS-66F; and diagrams of x-ray energy at locations 1A; and 2A. XBB 788-10564

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