

U.S. DEPARTMENT OF THE INTERIOR
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CA-MG CARBONATE DEPOSITS, WARNICK CANYON, COLUSA COUNTY,
CALIFORNIA

by

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ABSTRACT

Calcium-magnesium carbonate minerals occur as conglomerate cement and travertine within the sedimentary rocks of the upper plate of the Coast Range Thrust. The carbonate deposits of this study are located within Warnick Canyon, Colusa County, California, and occur within the lowest kilometer of the canyon. The mineralogy of the carbonates ranges from aragonite, calcite, Mg-rich calcite, and disordered dolomite. Water temperatures range from 18 to 23°C and pH values from 7.2 to 8.8. Chemically, the waters are mixed Na-Cl and Mg-HCO₃ type-waters.

INTRODUCTION

Ubiquitous Ca-Mg carbonate deposits (travertine and conglomerate cements) occur within the lowest kilometer of the Warnick Canyon in the Coast Range, Colusa County, California (Figure 1). The deposits are located in the ephemeral streambed and crop out on the west flank of the canyon. Carbonate specimens were collected from 4 sites (locations) in order to study their mineralogy, chemical composition, and morphology. Water, either from springs in contact with the carbonate deposits or flowing in the streambed, was collected from 4 sites at or near the carbonate deposits. The water was analyzed for major chemical constituents and water isotopic compositions.

Few studies of Ca-Mg carbonates from fresh water continental terrains have been reported. The early research by Arnold and Anderson (1908) entailed descriptions and interpretations of Ca-Mg carbonates located in the valley of White Creek near Coalinga, California. They reported that the water of White Creek emanated from serpentine terraces as springs with chemical compositions indicative of waters that had reacted with the host rocks at depth. The carbonates formed as a result of evaporation of the stream water as it flowed downstream. Barnes and O'Neil (1971) reported chemical and isotopic compositions of fluids and Ca-Mg carbonates of Holocene cements and travertine from the California Coast Range. The formation of Ca-Mg carbonates in the stream channels of the Coast Range was postulated by Barnes and O'Neil (1971) to result from primary precipitation of solutions formed by the dispersion of Ca-rich solutions into CO₃-rich solutions.

Many Ca-Mg carbonate deposits are known to be associated with economically important mineralized and geothermal regimes (for example, Barnes and others, 1973). This preliminary report presents the mineralogical and chemical data of carbonate minerals, together with stable isotopic and chemical data of waters samples collected between 9-91 and 4-92 from Warnick Canyon. This is the first part of a larger study of Mg-Ca carbonate deposits of the Coast Range.

ACKNOWLEDGMENTS

We thank Mr. Harold Pearson for permission to access his property. Without his assistance this study would not have progressed. Mark Huebner, United States Geological Survey (USGS), was instrumental in support during both the field sampling and laboratory analyses, and his talents are greatly appreciated. We also appreciate Terry Keith and Michael Thompson for their critical reviews of the manuscript. We thank Robert Mariner, USGS, for performing the X-ray diffraction analyses.

REGIONAL GEOLOGY

The entrance to Warnick Canyon is located at latitude, 39° 01' N and longitude, 122° 23' W and the canyon extends approximately 2 km northward (Figure 1). Located about 40 km southwest of Williams, the canyon lies in the southeast corner of the geologically complex Wilbur Springs structure (Lawton, 1956). The geologic structure of the region is represented by the juxtaposition of the Franciscan complex, the Coast Range Ophiolite, and the Great Valley Sequence (McLaughlin, et al., 1990). The area is crosscut by the Resort fault zone and is bounded by two northwest to northeast trending fault systems: the Bartlette Springs fault zone on the west and by the Bear Valley fault zone on the east (Lawton, 1956 ; McLaughlin, et al, 1990). The mouth of the canyon lies just to the northeast of the Resort fault zone. The canyon formed within the eroded rocks of the Great Valley Sequence (McLaughlin, et al., 1990). The Ca-Mg carbonate deposits of this study occur within the shales, mudstones, and lithic sandstones of the upper plate of the Coast Range thrust which is structurally underlain by detrital serpentinites. The more resistant serpentinites form the ridges of the canyon and their weathering products occur as clasts within the Ca-Mg carbonate conglomerates.

MINERALOGY

METHODS:

Hand specimens were collected from outcrops and streambed cements along the lower flanks and reaches of Warnick Canyon a tributary to Bear Creek. Five general sites are described that are representative of distinct local geochemical settings. The carbonate specimens were analyzed for mineralogical and chemical composition using X-ray diffraction (XRD) and energy-dispersive X-ray analysis (EDX). Elemental compositions, morphologies, and relationships of different carbonates within the same sample were documented using scanning electron imaging (SEM). Selected samples were also analyzed using backscattered electron image (BSE). Hand specimens were reduced in size mechanically to pieces no larger than 2 cm and were treated as single grain mounts. Specimens were mounted on aluminum stubs with conductive adhesive for observations and analysis with the SEM and EDX. Each sample was oriented so that the area of interest was clearly visible under a binocular microscope. All samples were coated with carbon for SEM analyses. If adequate photomicrographs could not be obtained because of sample charging, then a coating of gold/palladium was applied.

SITE LOCATIONS AND DATA:

Data applicable to the mineralogy of the carbonates in this study are presented under the sites where the samples were collected. Water samples from springs and flowing stream water were gathered at the time of mineral specimen collection whenever available or at nearby sites. The water data are presented in Table 1.

Site A

The carbonate deposit at site A (Figure 1) crops out on the west flank of Warnick Canyon about 20 m above the stream channel in partially exposed terraces (4) containing travertines and conglomerate cements (Figure 2). Thicknesses of the terraces are approximately one meter and individually they extend laterally no more than 5 m. The entire sequence extends about 15 m and slopes at about 35° towards the streambed, indicating a slump feature. No fluids were present at this outcrop during the collection period of this study. Figure 3 shows the texture and typical lithic fragments within the carbonate cement of the deposit. Figure 3b is a SEM BSE micrograph of cement and serpentinite clasts within the cement from site A. The variable MgCO_3 composition of the carbonates from site A are shown on the diffractograms together with the relative amounts of aragonite and other minor minerals (Figure 4a and 4b). The elemental compositions of the Ca-Mg carbonates of site A are shown on Figure 5a and 5b.

Site B

Site B is located on the west side of the stream bed and is situated below and 10 m downstream of site A (Figure 1). During the collection period of our study, groundwater at this site flowed from a spring beneath the exposed carbonate lenses that were lithologically similar to the travertines and conglomerates at site A. These lenses are roughly horizontal and are about 15 m long and 1 m thick (Figure 6). At the base of the outcrop, halite occurs and the Ca-Mg carbonate beds are in direct contact with the site B spring (Figure 7). The diffractogram for the Ca-Mg carbonates at site B shows that Mg compositions are similar to those at site A and appear to be near dolomite in MgCO_3 composition (Figure 8). At site B, silver and nickel were observed as discrete phases in the carbonate cement together with Cl and Si (Figure 9). Even though nickel and chromium occur in the lithic serpentinite fragments in the carbonate cements (Figure 10a and 10b), the silver and nickel were determined by EDX to be chloride salts in the Ca-Mg carbonate cements (Figure 9). Elemental titanium was also identified by EDX in the Ca-Mg carbonate cement from site B. No investigative study was done to quantify any of these metals.

Site C

No carbonate specimens were found at this location. Water samples collected at this site emanates from fractured bedrock in the stream bed.

Site D

Site D is located approximately 40 m downstream from site A (Figure 1). The site is approximately 20 m above the stream bed on the west flank of the canyon (Figure 1). The exposed conglomerate is lithologically similar to the conglomerate at site A (Figure 11). The outcrop is <1 m thick and approximately 2 m in length. The outcrop is part of the general slump feature of the hillside. During the collection period of this study no fluids were observed at site D. The MgCO_3 composition of the carbonate cement at site D is indicated by the diffractogram as shown on Figure 12. The elemental composition of the carbonate at site D, shown on Figure 13, supports the presence of the MgCO_3 component shown on the corresponding diffractogram (Figure 12).

Site E

No carbonate specimens were found at this location. Water samples collected at this site emanates from fractured bedrock in the stream bed.

Site F

Site F is located at the mouth of Warnick Canyon. Samples were collected from the apron that is forming on the north bank of Bear Creek (Figure 1). The apron is approximately 3m thick, 10 m wide, and 5 m in length (Figure 14). The carbonate mineralogy at site F varies from aragonite to disordered dolomite. Figures 15a and 15b show diffractograms of the carbonates at site F. Typically, aragonite thinly coats the top surface of the apron (Figure 16) and also coats the galleries formed within eroded portions of the apron (Figure 17). The SEM micrographs of aragonite and the Ca-Mg carbonates of site F are shown on Figures 18 and 19, respectively. Lastly, Ni and Cl occur in the elemental composition of the carbonate cement determined by EDX as shown on Figure 20.

WATER CHEMISTRY

Methods: The methods utilized for field determination of pH and laboratory sample preparation are described in Presser and Barnes (1985). Alkalinity concentrations were determined by titration with acid on an automatic titrator. The alkalinity was determined on samples collected in bottles completely filled, sealed with polyseal caps, and stored under refrigeration. Chloride concentrations were estimated using a silver dichromate indicator strip ($\pm 4\%$). Sulfate concentrations were estimated using turbidimetric readings of precipitated barium sulfate solutions. Cations, silica, and boron were analyzed by inductively coupled plasma ($\pm 2\%$).

Table 1. Chemical composition of waters from Warnick Canyon. Concentrations in mg/L. Temperatures of samples were approximately 18 to 23°C. SO₄ concentrations ranged from 20 to 25 mg/L.

Sample	pH	Na	K	Mg	Ca	Li	Ba	HCO ₃	Sr	Cl	B	SiO ₂
						<u>Site B</u>						
123-91	7.74	3,600	160	620	96	15	4.5	2,250	22	5,900	260	58
099-91	7.25	3,650	175	585	96	14	4.3	2,200	20	6,000	260	66
128-91	7.93	3,600	150	630	84	14	3.0	2,300	22	6,750	260	54
130-91	7.75	3,750	160	620	100	14	3.3	nd	21	5,900	nd	57
136-91	7.64	3,750	165	635	100	15	3.4	2,300	22	5,900	260	57
142-91	7.99	3,750	150	630	81	14	4.3	nd	21	6,000	270	45
292-92	7.42	3,500	165	570	80	15	5.0	nd	20	5,800	265	66
295-92	7.42	3,450	165	550	88	15	3.9	2,050	19	5,300	260	62
337-92	7.70	3,200	145	490	78	13	3.0	1,900	17	5,300	230	61
						<u>Site C</u>						
098-91	8.25	6,300	265	905	53	23	3.9	2,850	23	11,500	410	40
100-91	8.40	6,750	285	950	82	25	4.3	2,900	25	12,500	450	28
122-91	8.49	16,000	585	2,050	120	57	4.4	2,700	51	30,500	640	7
129-91	8.50	23,000	735	3,150	150	76	4.2	3,500	66	42,500	830	6
141-91	8.79	4,900	205	625	43	18	1.0	nd	14	8,000	330	9
291-92	7.90	3,500	160	560	85	16	3.2	nd	19	5,300	280	51
294-92	8.31	3,750	195	555	79	16	2.5	nd	18	6,300	310	40
						<u>Site E</u>						
131-91	8.01	4,600	190	825	97		6.9	3,050	26	8,650	295	26
137-91	7.94	4,850	210	855	90		4.3	nd	24	8,650	310	57
						<u>Site F</u>						
124-91	8.60	2,650	81	750	140		0.6	1,500	14	4,750	180	20

ISOTOPES

Methods: Stable isotope analyses were performed on water samples collected at the field sites in 15 mL glass bottles with polyseal caps. The oxygen isotopic compositions of waters were determined by analyzing CO_2 which had been equilibrated with these solutions at 25°C (Epstein and Mayeda, 1953). The hydrogen isotopic compositions were determined on H_2 produced during reduction of water over Zn at 450°C in 6 mm glass tubes with a precision of ± 1 permil (W.W. Carothers and R.H. Brigham, unpublished method). Dissolved CO_2 species were precipitated in the field by adding 20 mL saturated ammoniacal SrCl_2 to approximately 100 mL of water. Prior to isotopic analysis for $\delta^{13}\text{C}$ values, the SrCO_3 precipitates were filtered and washed under a CO_2 free atmosphere, dried, and homogenized in a ball mill. The precipitates were reacted with $>100\%$ H_3PO_4 at 25°C and the evolved CO_2 collected for isotopic analysis (McCrea, 1950). All isotopic measurements for oxygen and hydrogen are reported in Table 2 in permil deviations relative to SMOW (Standard Mean Ocean Water). The $\delta^{13}\text{C}$ values are reported relative to PDB (Chicago Peedee belemnite standard). The precision of a single measurement is ± 0.1 permil for oxygen and carbon values.

Table 2. Isotopic composition of waters and dissolved inorganic carbon species from Warnick Canyon.

Sample	Date collected	$\delta^{18}\text{O}$	δD	$\delta^{13}\text{C}$
<u>Site B</u>				
123-91	11/22/91	2.8	-30.5	8.4
099-91	8/16/91	2.4	-32	6.1
128-91	11/22/91	2.4	-34	7.4
130-91	12/6/91	2.6	-33.5	8.4
136-91	12/6/91	2.5	-33.5	7.5
142-91	12/28/91	-0.3	-43	
292-92	2/27/92	2.3	-33	
295-92	2/27/92	2.2	-36	
337-92	3/20/92	1.7	-33	
<u>Site C</u>				
098-91	8/16/91	5.3	-20	
100-91	8/16/91	6.5	-13	
122-91	11/22/91	2.0	-15.5	-0.1
129-91	11/22/91	1.8	-20.5	2.3
141-91	12/28/91	-8.3	-74	
291-92	2/27/92	2.0	-34	
294-92	2/27/92	2.0	-32	
<u>Site E</u>				
131-91	12/6/91	2.2	-35	6.4
137-91	12/6/91	2.1	-35	5.6
<u>Site F</u>				
124-91	11/22/91	1.8	-22.5	-3.0

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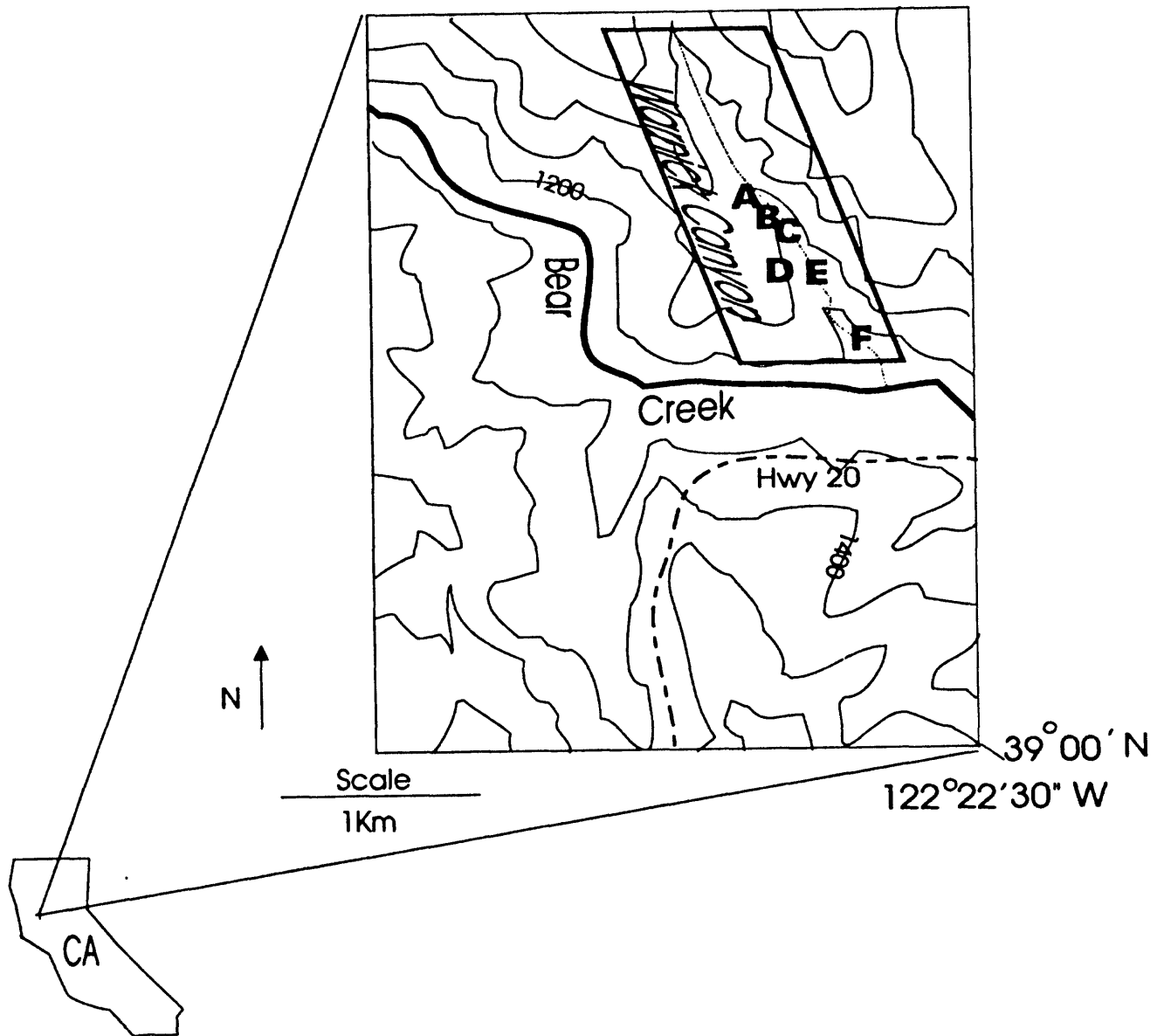


Figure 1. Location map of Warnick Canyon showing sample sites. Contour intervals are 200 feet.



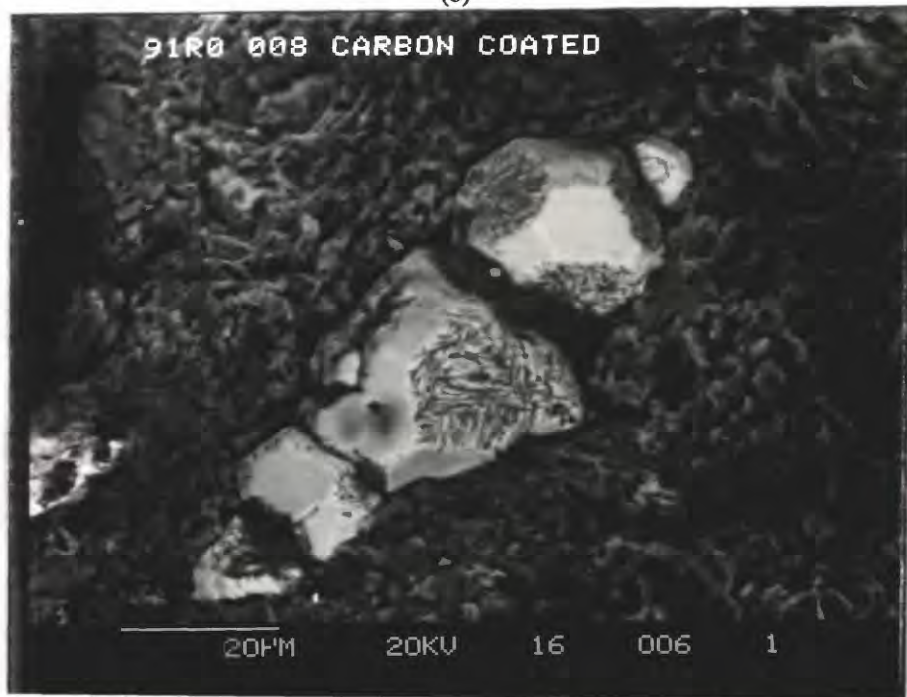
Figure 2. Photograph of site A. Ca-Mg carbonate cement of the conglomerate is located approximately 20 m above the stream channel. The thickness of the conglomerate varies and can be as much as a meter. Exposed bedding planes of conglomerate are typical. 14 x 20 cm sample bag for scale.



(a)

Figure 3. (a) Photograph of conglomerate from site A. Lithic fragments that cap the high points are well exposed on this weathered surface. Pocket knife for scale. (b) SEM BSE image of subhedral serpentinite clasts (light) within the carbonate matrix (dark) from site A.

(b)



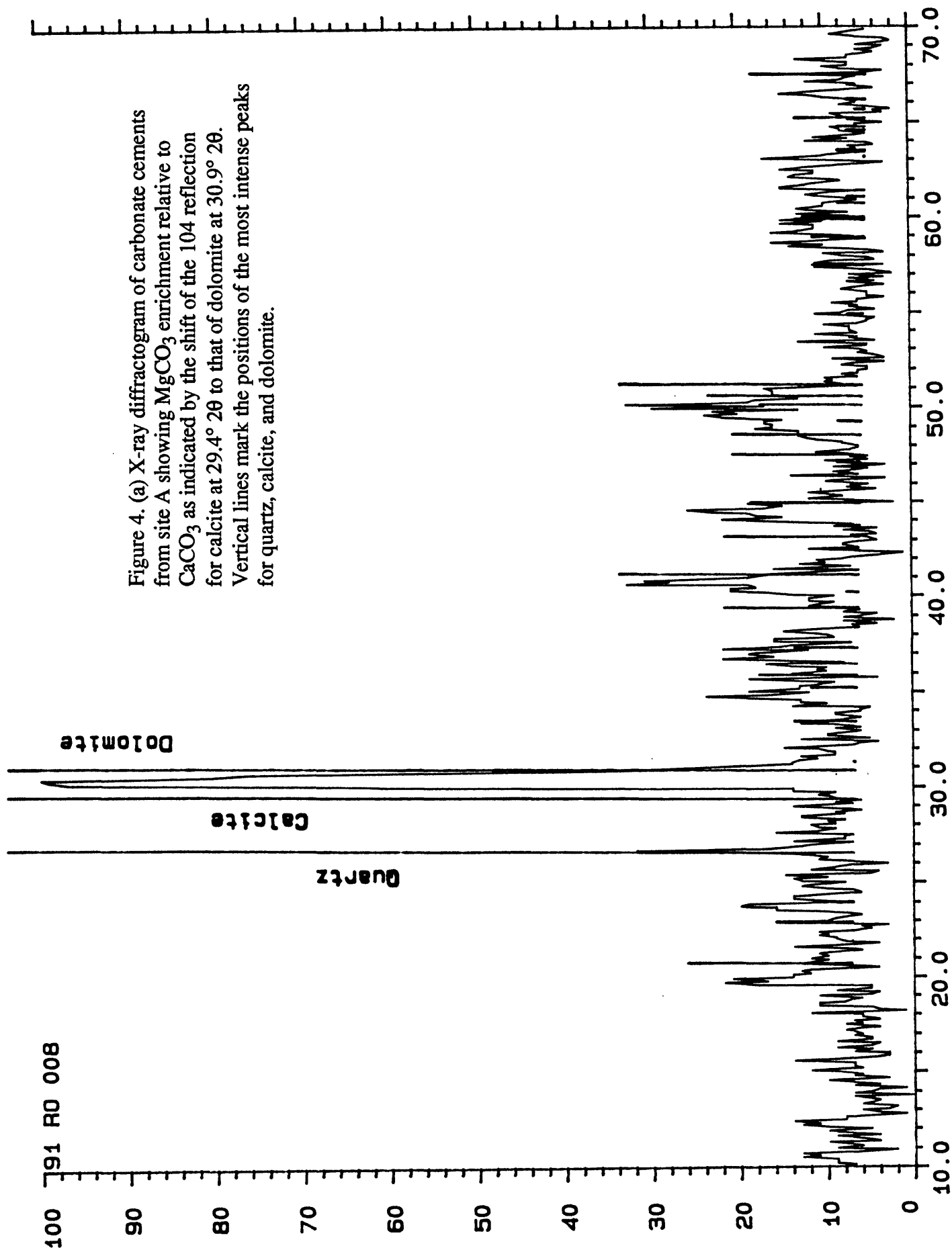


Figure 4. (a) X-ray diffractogram of carbonate cements from site A showing MgCO_3 enrichment relative to CaCO_3 as indicated by the shift of the 104 reflection for calcite at $29.4^\circ 2\theta$ to that of dolomite at $30.9^\circ 2\theta$. Vertical lines mark the positions of the most intense peaks for quartz, calcite, and dolomite.

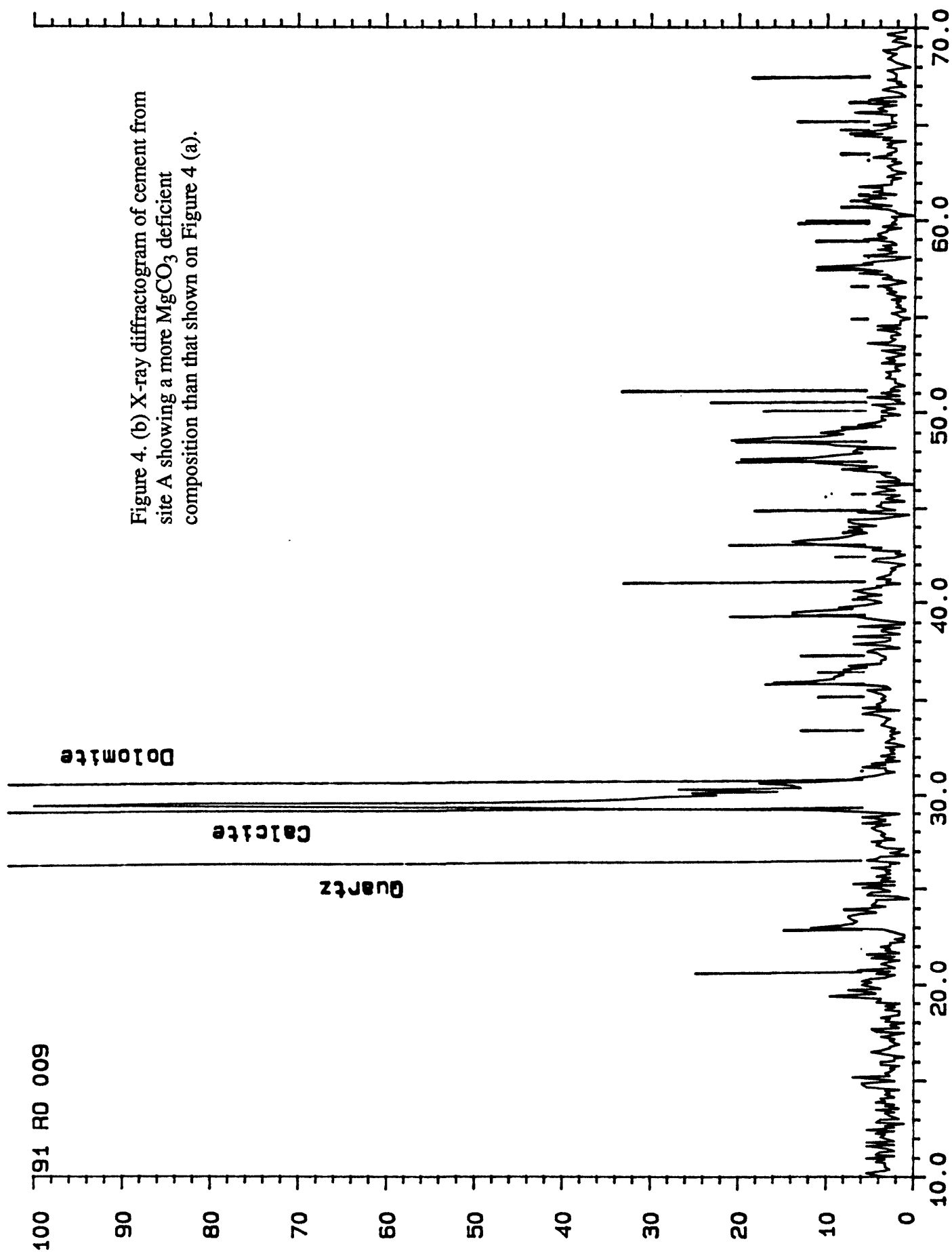


Figure 4. (b) X-ray diffractogram of cement from site A showing a more MgCO_3 deficient composition than that shown on Figure 4 (a).

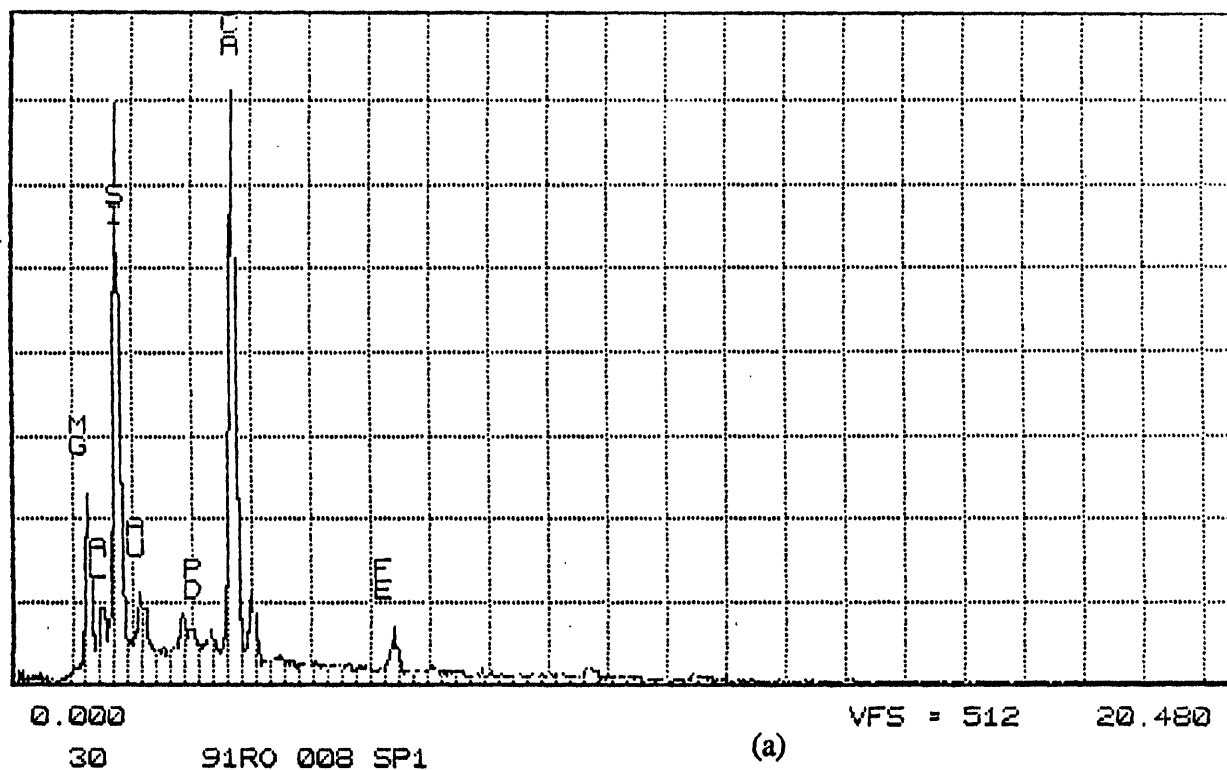


Figure 5. (a) EDX spectral print-out of Ca-Mg carbonate cement from site A shown on Figure 4a. Note presence of Si and Fe: Au and Pd are from the sample coating. (b) EDX spectral print-out for cement shown on Figure 4b which shows depletion of Mg relative to that shown on the spectral print-out for (a). Note absence of Si and Fe.

(b)

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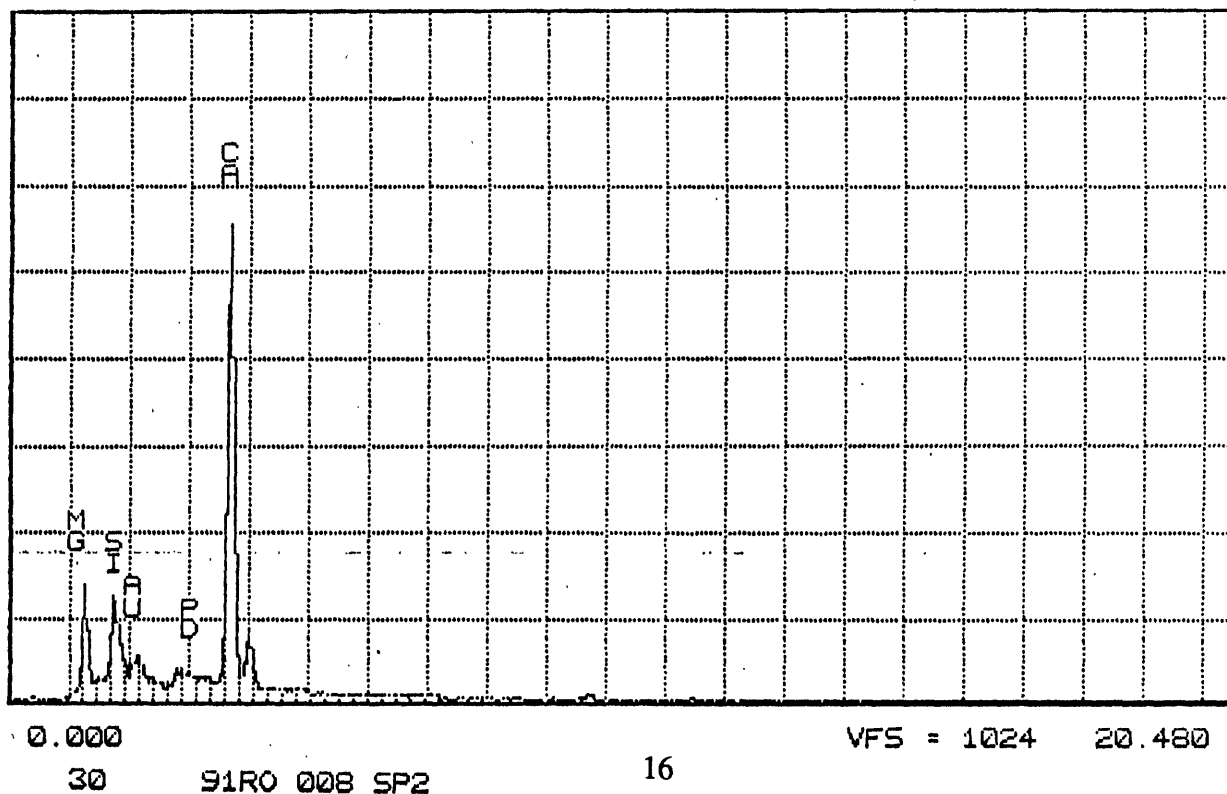




Figure 6. Photograph of site B. Site B is located in the main channel and about 10 m downstream of site A. The spring flows from beneath the conglomerate beds that are roughly horizontal and about 15 m in length.



Figure 7. Close-up photograph of site B. This photograph shows the halite-bearing horizons (areas of white to light brown) in the Ca-Mg conglomerate beds just above the spring.

191 RO 012

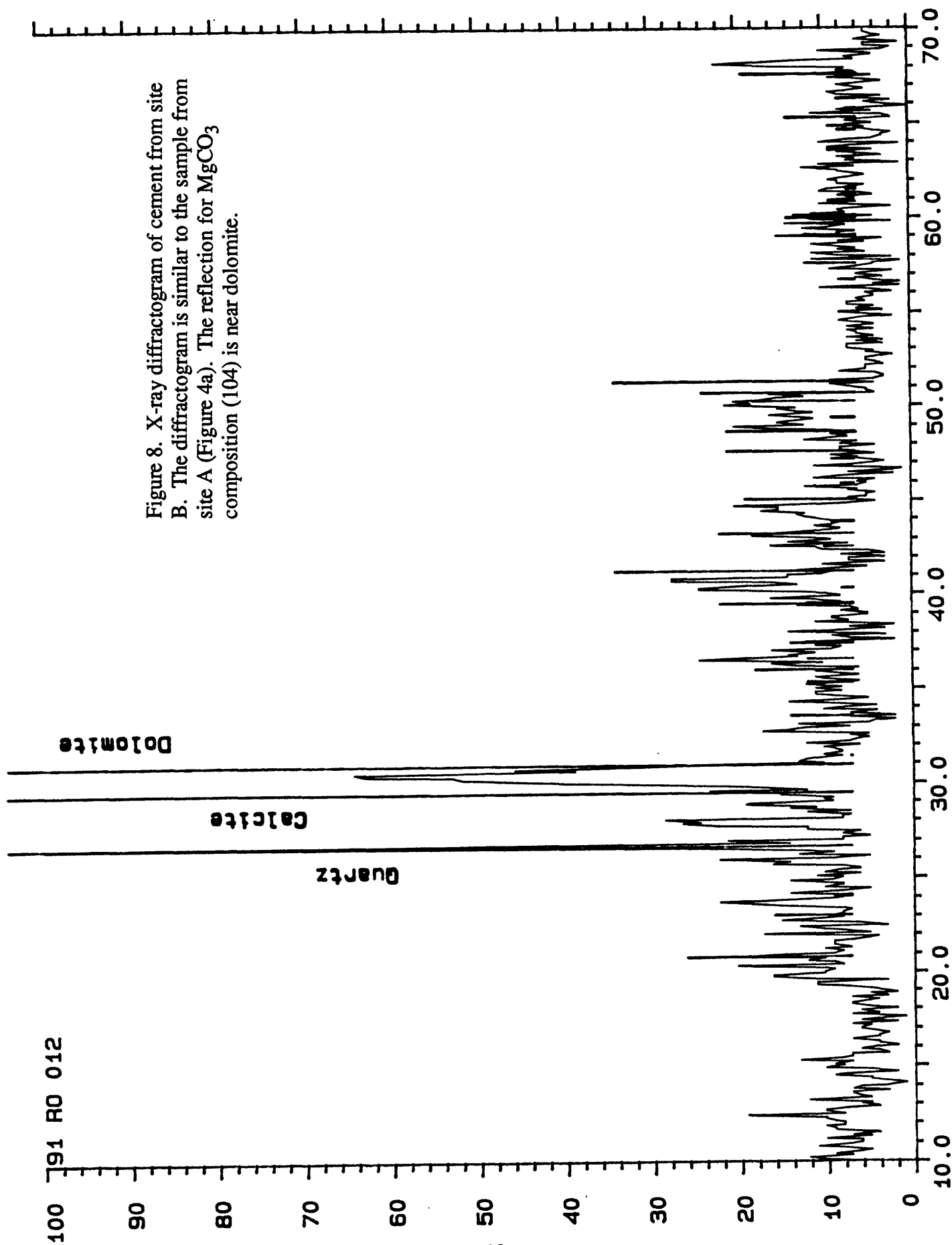


Figure 8. X-ray diffractogram of cement from site B. The diffractogram is similar to the sample from site A (Figure 4a). The reflection for MgCO_3 composition (104) is near dolomite.

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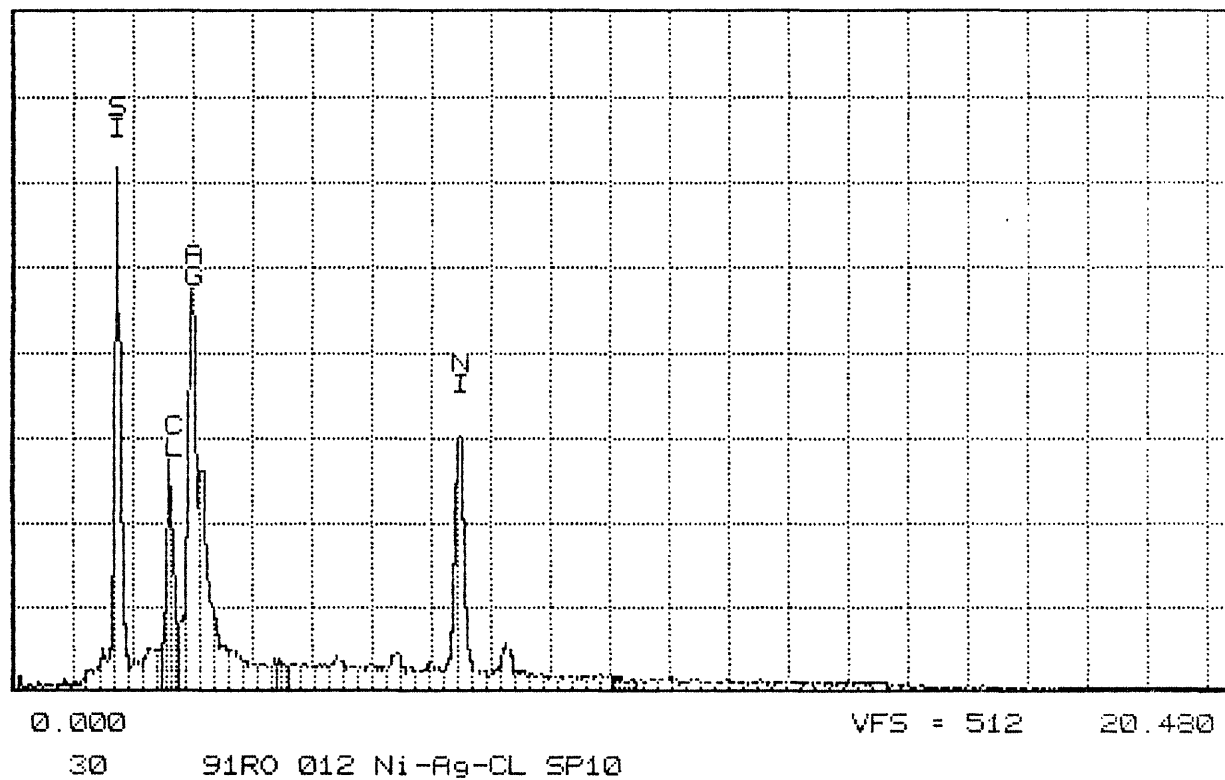
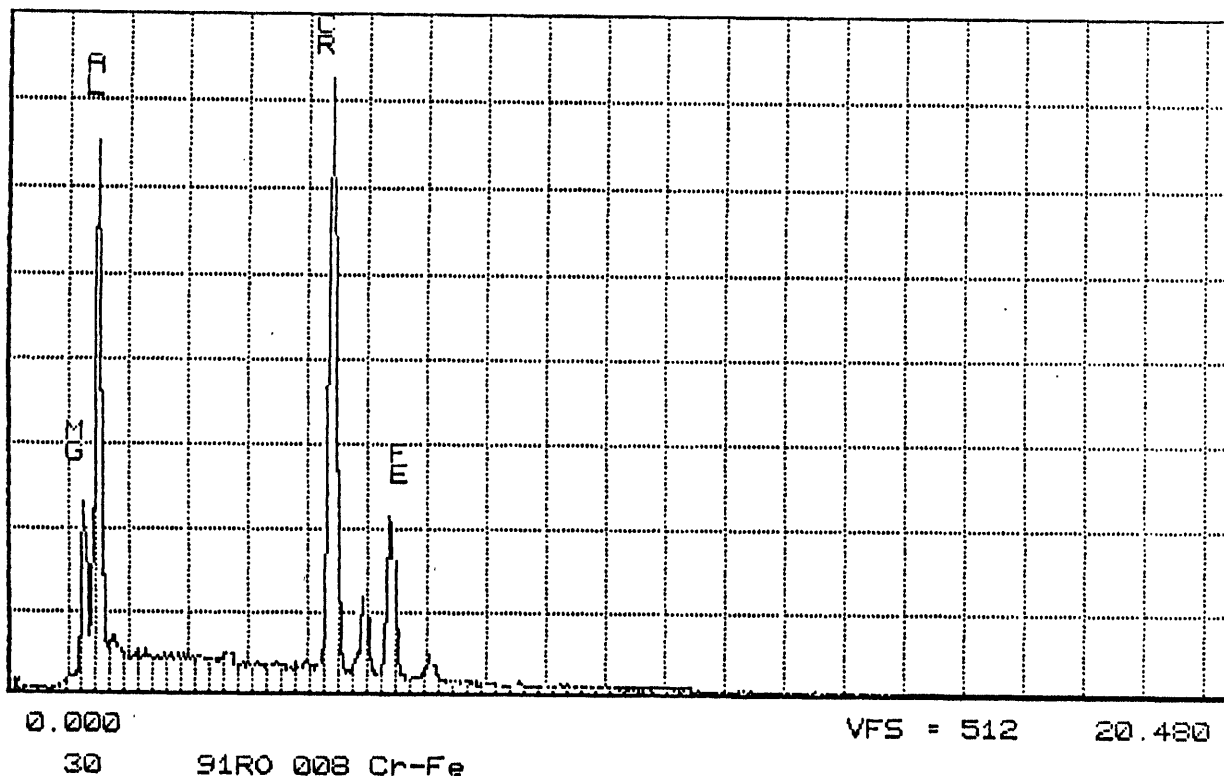


Figure 9. SEM EDX elemental spectrum showing the presence of Ag and Ni with Cl and Si in a sample from site B.



(a)

Figure 10. (a) and (b) SEM EDX spectrums showing the presence of Cr (a) and Ni (b) along with Mg and Al from serpentinite fragments from site B (a) and fresh sample of serpentine boulder from Bear Creek (b).

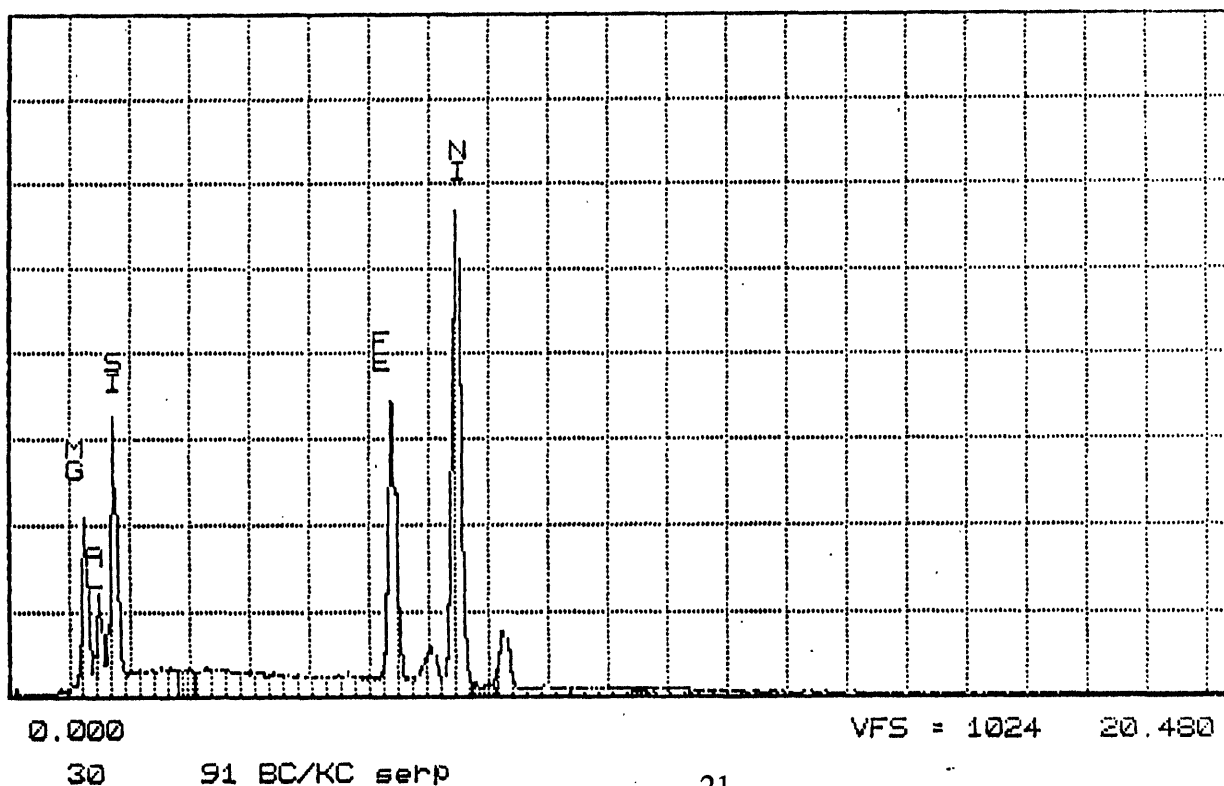
(b)

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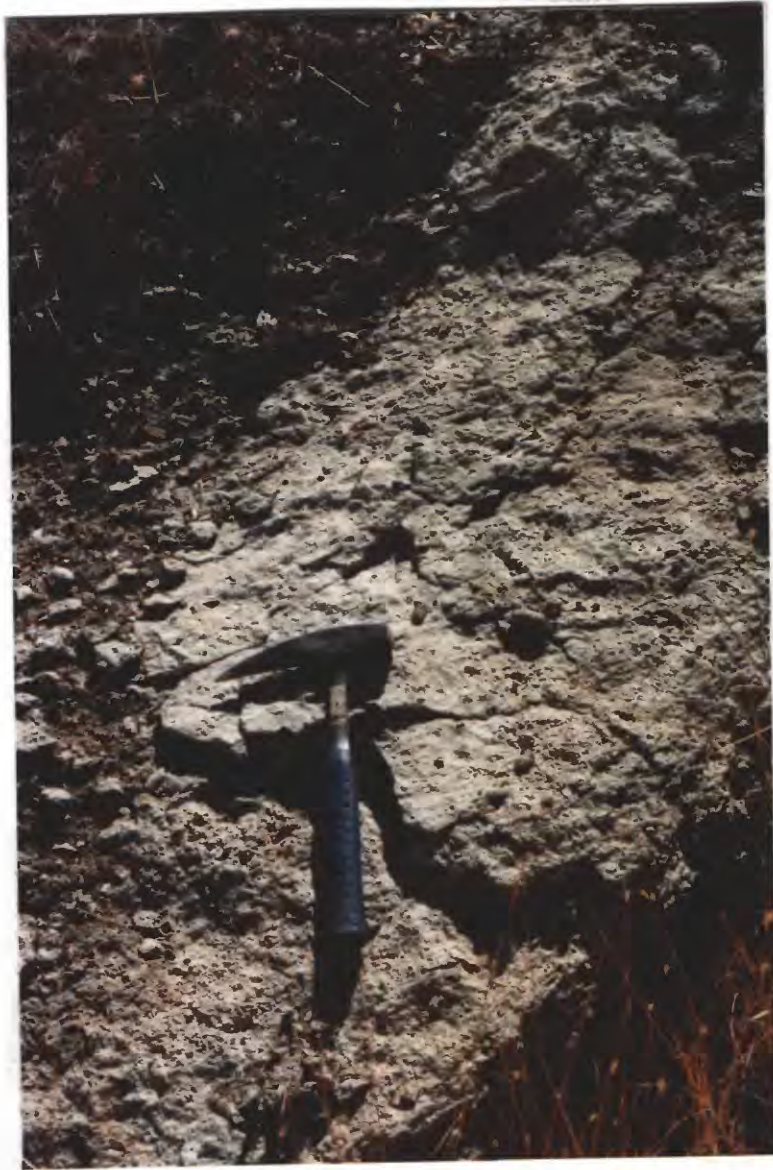


Figure 11. Close-up photograph of site D. This outcrop is located about 40 m downstream from site A and is also situated on the west flank of the canyon. The conglomerate is in every way similar to the conglomerate at site A.

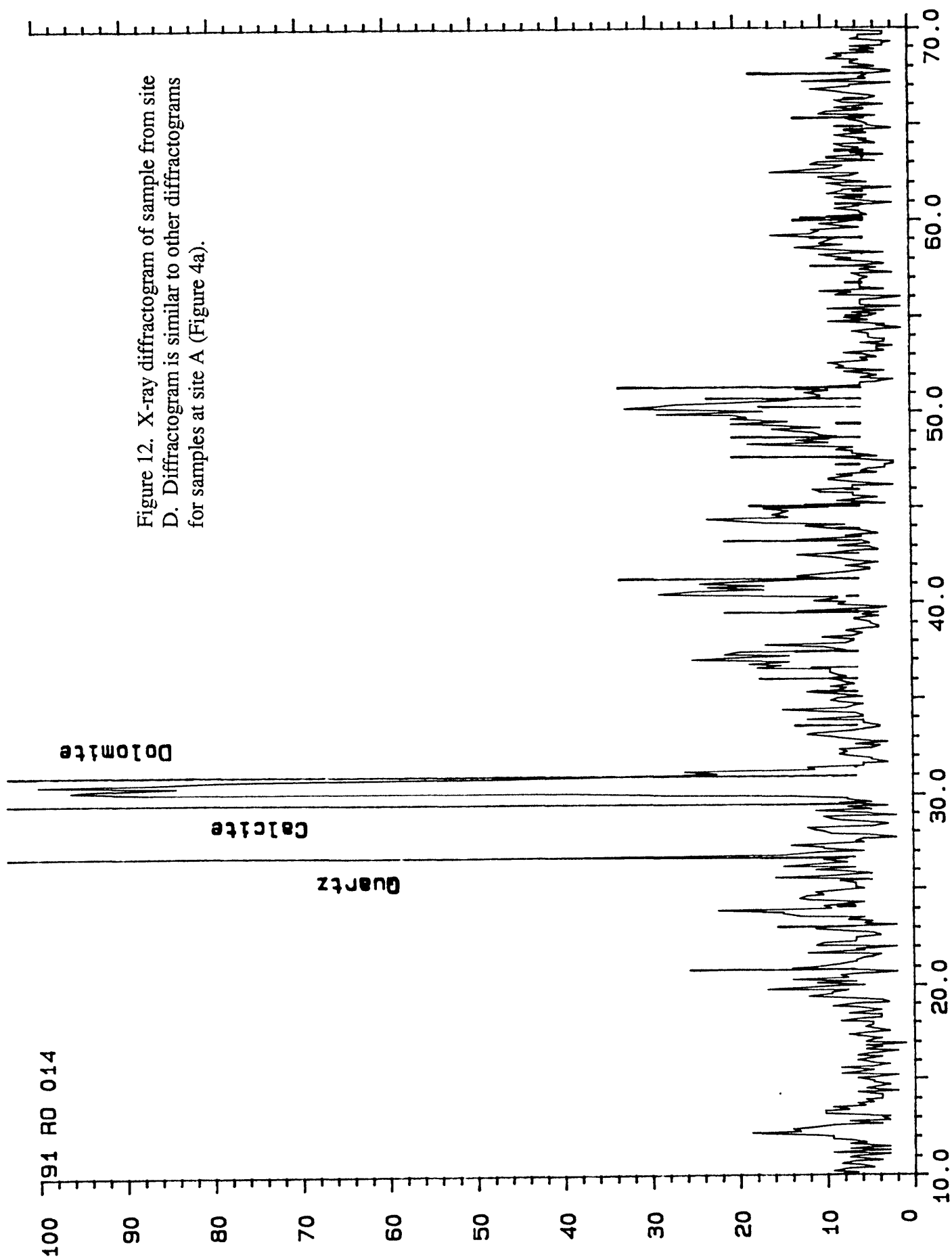


Figure 12. X-ray diffractogram of sample from site D. Diffractogram is similar to other diffractograms for samples at site A (Figure 4a).

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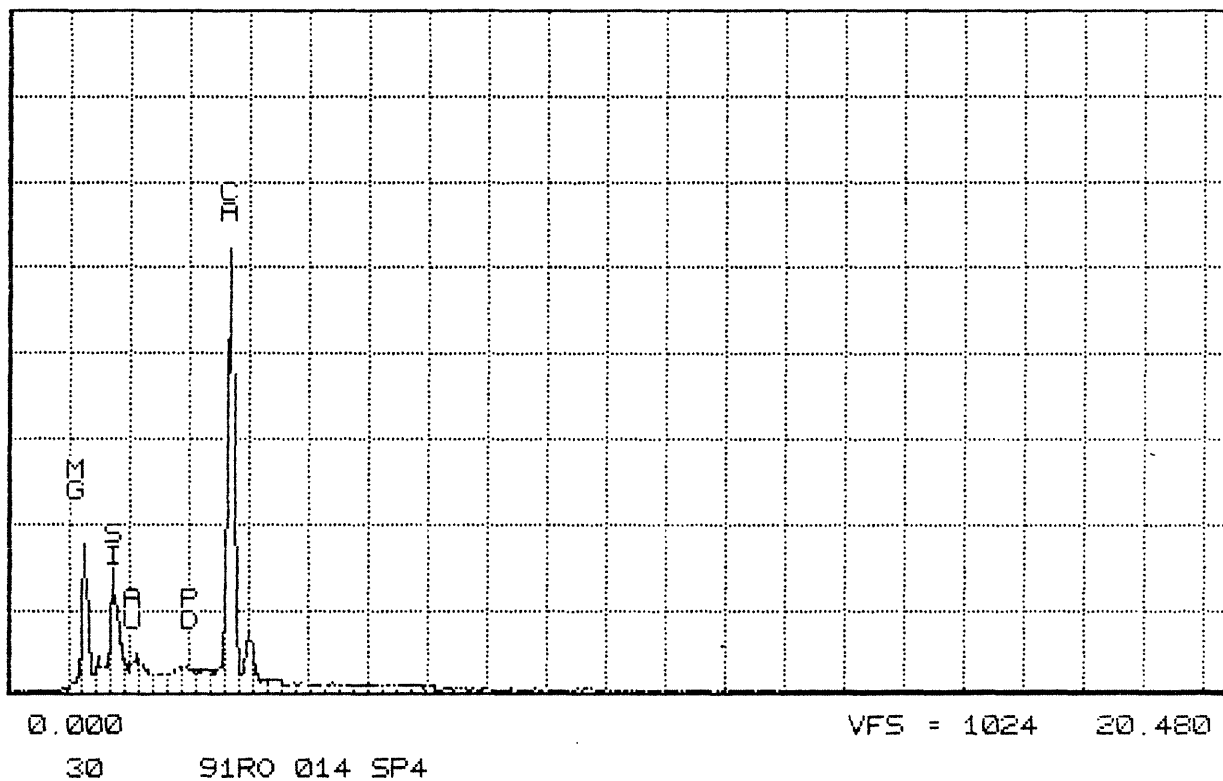


Figure 13. SEM EDX elemental spectrum of sample from site D. Note MgCO_3 -rich composition of the carbonate.



Figure 14. Photograph of site F looking southeast from the mouth of Warnick Canyon showing Bear Creek. The white coating is fresh evaporite (aragonite) that formed after the last rain. The top of the apron lies about 5 m above the level of Bear Creek.

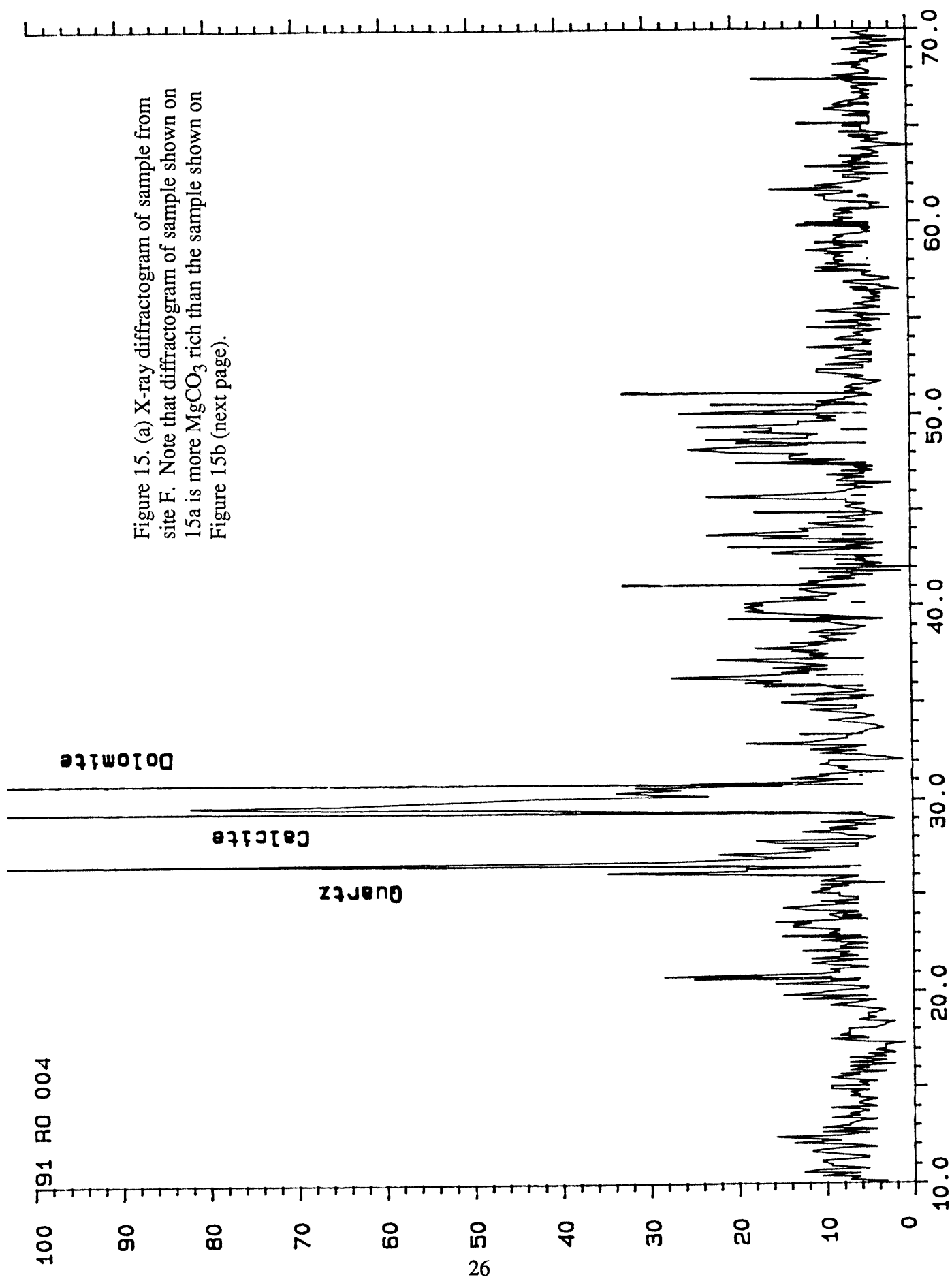


Figure 15. (a) X-ray diffractogram of sample from site F. Note that diffractogram of sample shown on 15a is more MgCO_3 rich than the sample shown on Figure 15b (next page).

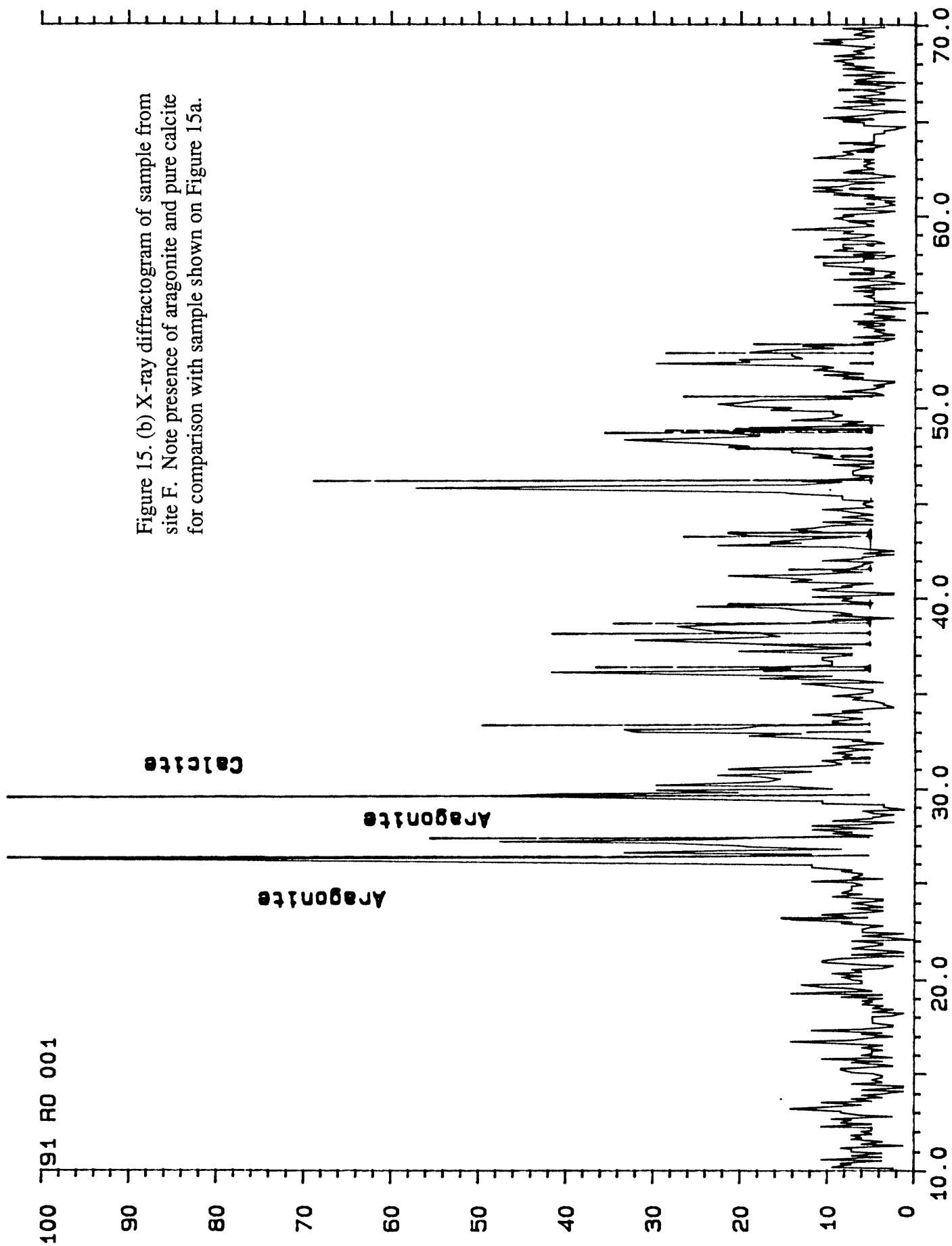


Figure 15. (b) X-ray diffractogram of sample from site F. Note presence of aragonite and pure calcite for comparison with sample shown on Figure 15a.



Figure 16. Close-up photograph of the top surface of the apron (Figure 14) showing a thin coating of aragonite. Hammer shown for scale.

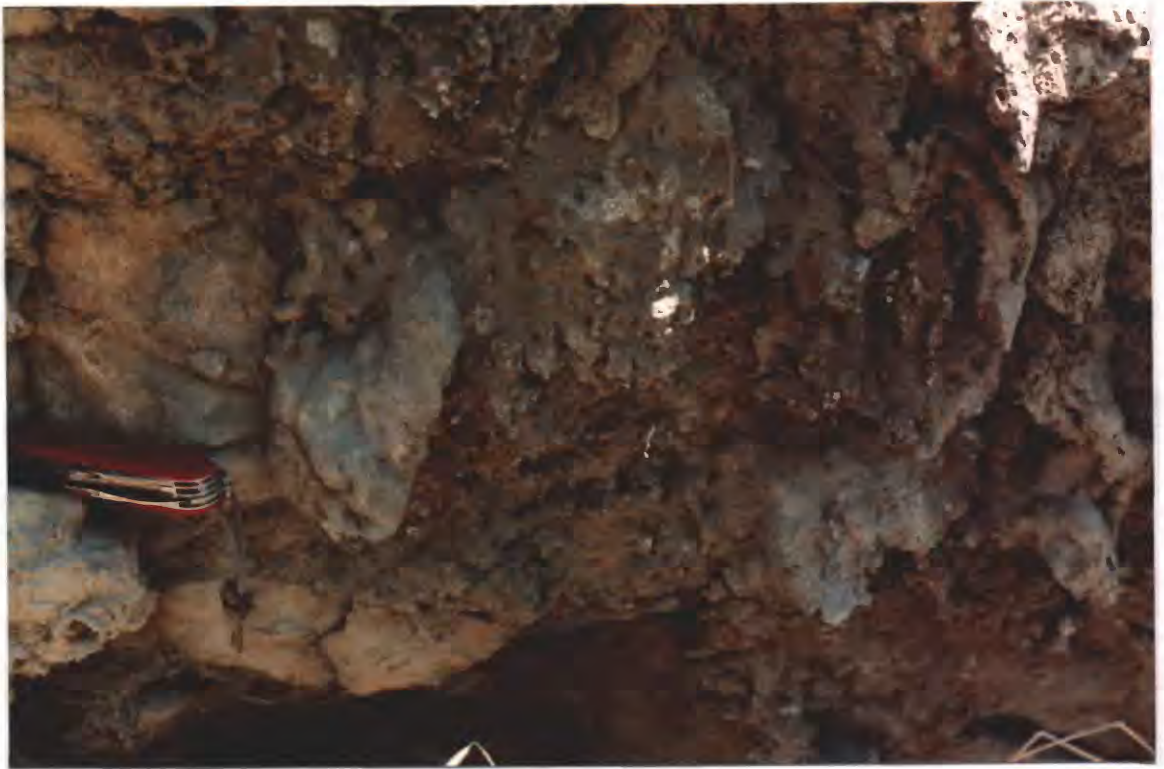


Figure 17. Photograph of site F. This photograph was taken on the north flank of the apron and shows the aragonite coating. Also shown is the aragonite coating of small stalactites exposed in the eroded galleries of the deposit.

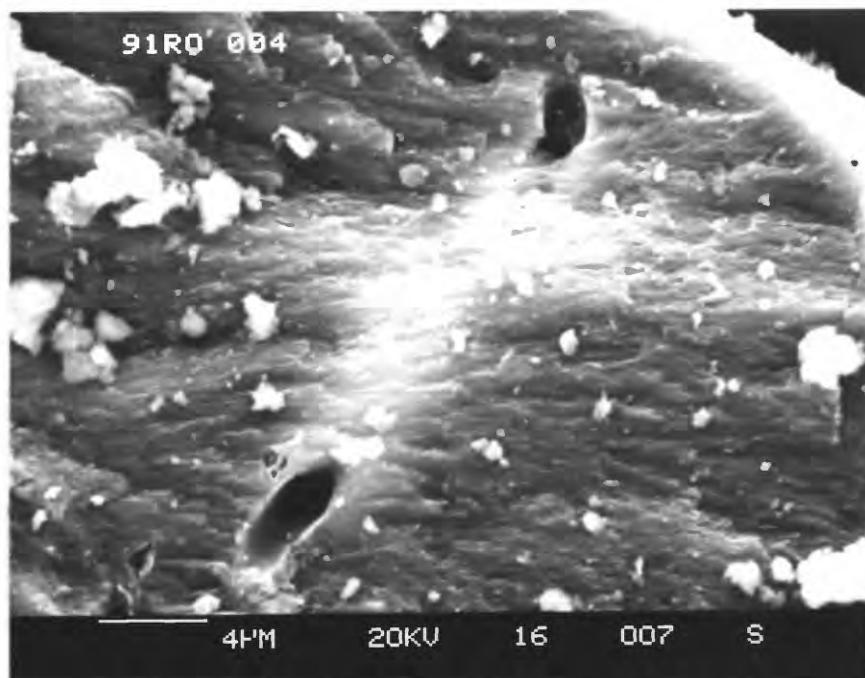


Figure 18. SEM micrograph of the aragonite surface of a sample from site F. Holes may indicate the presence of vegetation during crystal formation. The organic material has disintegrated and left a clear opening.

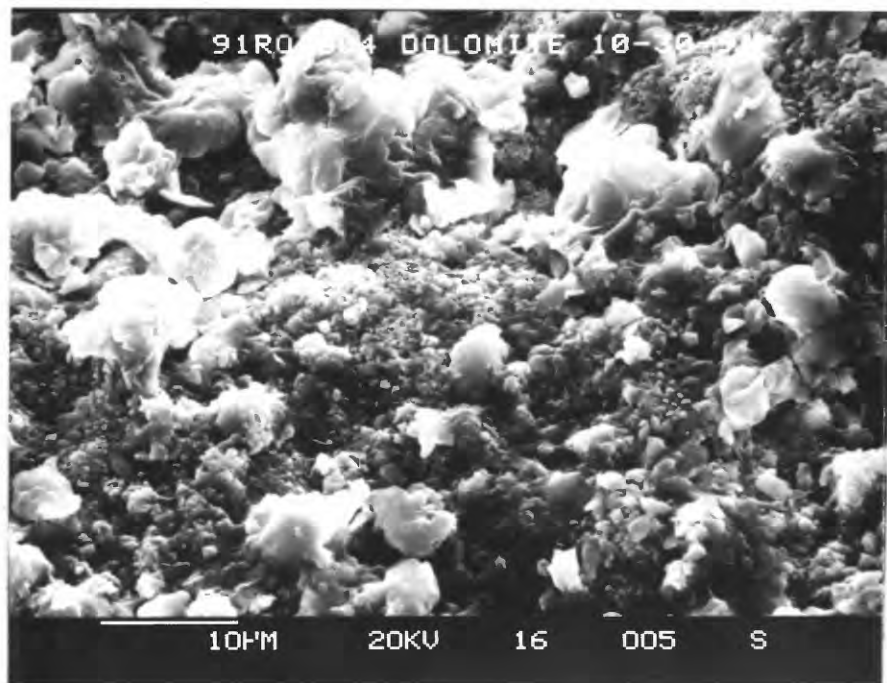


Figure 19. SEM micrograph of Ca-Mg carbonate (dolomitic) from site F. Micrograph shows the incipient dolomite grains.

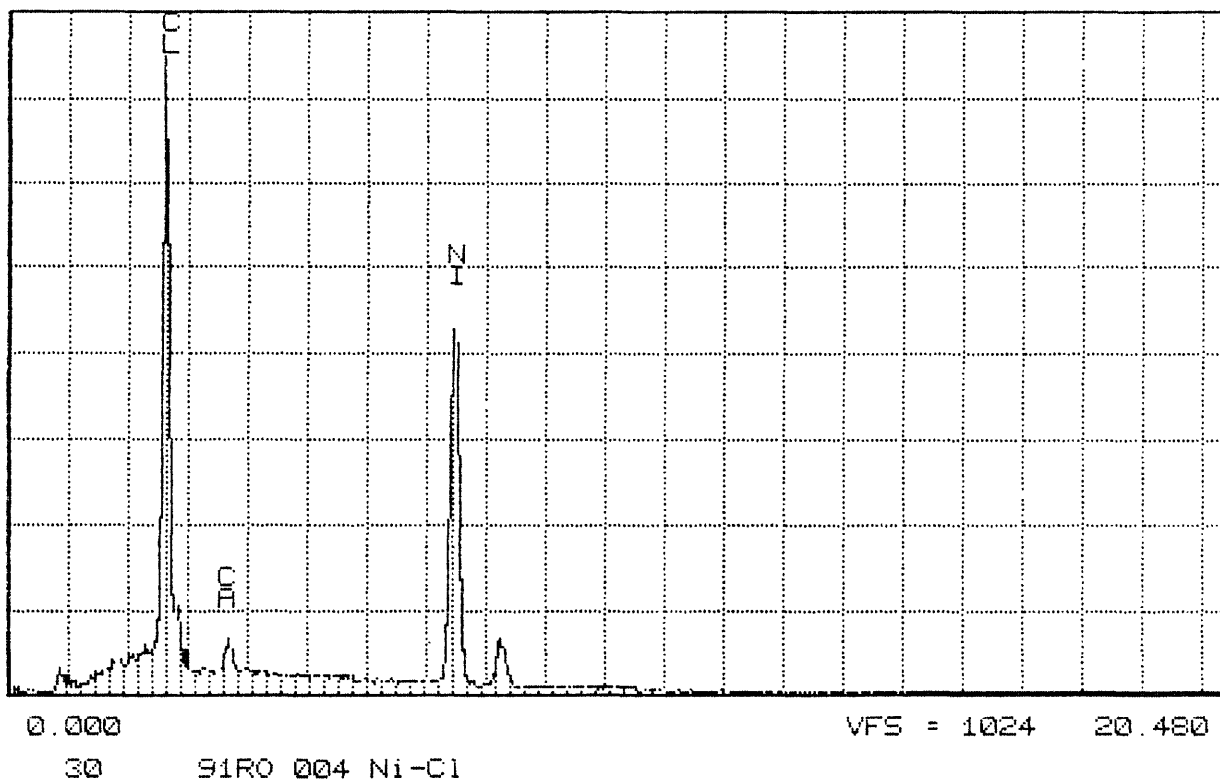


Figure 20. SEM EDX elemental spectrum of carbonate matrix for a sample from site F showing presence of Ni and Cl.