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# Mineralogy of the

# KALKAR QUARRY

## Santa Cruz, California



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The Kalkar quarry produced commercial limestone for nearly a century. It has also yielded 76 minerals, including several rare sulfosalts and silicates, and is the type locality for pabstite, the tin analog of benitoite. The mineralogy of this quarry is unique in the region, but unfortunately the locality is now essentially extinct.

#### INTRODUCTION

The Pacific Limestone Products Company quarry, locally known as the Kalkar quarry, is located in the coastal town of Santa Cruz, about 96 km south of San Francisco in the southwest quarter of Sec. 11, T11S, R2W, M.D.M. The company property is surrounded on the north by the University of California Santa Cruz campus, on the east by Spring Street, and on the south and west by private residences.

Limestone has been mined at the deposit since before 1884 (Hanks, 1884). The property was sold in 1922 to the Pacific Limestone Products Company. From this time until the mid 1960s, when the property was sold for real estate development, the company produced a variety of limestone products, the most common being livestock feed supplements and decorative stone.

The deposit has been developed by two quarries about 200 meters apart at an elevation of 100 meters above sea level. The larger and more recently active of the two quarries explored a massive recrystallized limestone and calc-silicate rock assemblage which has been faulted and broken. Solution cavities, although small, are common throughout the limestone body where calc-silicate rocks are absent. Underground water was a constant problem during quarry operations, and both channels and pumps have been used for drainage.

Mineralization is confined to the larger quarry and consists of a number of silicates related to contact metamorphism, followed by sulfide and sulfosalt replacement of the recrystallized limestone. Weathering of the sulfide-sulfosalt minerals has produced a large number of secondary minerals. Minerals identified from the quarry include native elements, sulfides, arsenides, sulfosalts, oxides, hydroxides, carbonates, sulfates, arsenates, phosphates, molybdates and silicates.

#### HISTORY

#### **Quarry Operation**

The earliest records of limestone quarrying operations date back to before 1884 (Hanks, 1884). The operations have been summarized by Hubbard (1943) for the years 1922 to 1943. The operations continued essentially unchanged from 1943 until the quarry ceased operation in the mid 1960s.

Basic quarry operations consisted of drilling charge holes in the massive limestone blocks and breaking them up with explosives. Air from a portable Schramm compressor operated several dry jackhammers using detachable bits. Pieces larger than 1 meter were plug shot and subsequently broken with 7 kg rock hammers to sizes less than 30 cm. Because of magnesium and silica impurities, all rock was hand-picked to insure uniform quality. The resulting rock was hand-loaded into special steel skips fitted with removable aprons operated from the truck driver's seat. These skips held about 1 to 1.5 metric tons of rock and had a lug in each side to fit hoisting hooks on the company's ingenious patented trucks, which were built on a Model A Ford chassis with a friction-drive cable



Figure 1. Panoramic view of the Kalkar quarry 1965. The mineralized western section is at left, the fault area is at center.

hoist employing a worm-drive rear axle assembly. The loaded skips containing limestone were transported to the nearby mill for processing. The impure material remaining was sold for building and decorative stone.

The processed limestone was sold for various applications including terrazo, stucco dash, chicken grit, roofing grit, commercial filler, mortar sand, cattle calcium, poultry calcium, fertilizer and macadam. The most important product, however, was a complex mineral mix for livestock and cattle.

#### **Mineral Collecting**

Fitch (1931) noted occurrences of a number of minerals in the irregular beds of limestone; these included quartz, diopside, forsterite, phlogophite, titanite, tourmaline, chlorite, arsenopyrite and pyrite. Later in the 1930s, Fred W. Johnson, owner of the quarry, called to the attention of the late Magnus Vonsen, (a skilled amateur mineralogist of the Bay area) the rare and interesting minerals which were being found during quarrying operations. Among the first rare minerals to be identified by Vonsen were meneghinite and franckeite (Gross *et al.*, 1967).

During the 1940s, Charles W. Chesterman, geologist for the California Division of Mines and Geology, and Charles Milton of the U.S.G.S. collected a small suite of minerals from the quarry which included meneghinite, franckeite, pyrrhotite, stannite, native bismuth, arsenopyrite and fluorapatite. In the following years the quarry was visited by a number of local mineral collectors who collected fine specimens of many different minerals.

In 1958 the authors became interested in the minerals that had been reported from the Kalkar quarry; during the next 12 years the quarry was visited regularly on weekends. On each visit a systematic examination of the quarry area was made for any new exposures of minerals. These occurrences were recorded along with data such as rock type, location, mineral content and associations. Since the quarry was actively being worked, both the overall quarry dimensions and the exposed mineralogy were constantly changing. To aid in mineral location within the quarry, a large plane table map of the quarry was constructed with a location grid system; each mineral find was recorded on the map with the date. The quarry was eventually divided into nine general collecting areas labeled A through I. These areas are located on the quarry map and the minerals occur-

ring at each location are listed in Table 1. Locations A through E are located in an area which was not being worked for limestone. Locations F through I are located in the north portion of the quarry where blasting was constantly exposing new rock.

Since blasting was usually performed on Friday afternoons, Saturday collecting was usually profitable because new rocks were exposed and the larger ones had been reduced to a manageable size. Quarry collecting usually consisted of examining the surfaces of each rock for exposed metallics and cavities which might contain minerals. Often the quarry was visited at night with a shortwave ultraviolet light.

The largest exposure of sulfide-bearing calc-silicate rocks was in the western part of the quarry and included locations A through D. Here the calc-silicate rocks are interstratified with beds of coarse-grained limestone. Within these rocks, masses of sulfides and sulfo-salts were regularly found associated with quartz, tremolite and actinolite. The high silica and heavy metal content of this rock made it unusable for commercial feed application or decorative stone because of its general lack of compactness and its weathering characteristics. Early quarry operations extracted only small quantities of limestone from this area, and in later years it was used as a dump for waste rock. During the early years abundant franckeite and meneghinite associated with pyrite and pyrrhotite were common in this area. Much of the quarry floor, however, is now covered with waste rock, trees, brush and water.

Locality A is a small sulfide-rich quartz vein near the processing plant. The exposed vein measures about 1 meter high and 50 cm wide, and dips slightly to the east. Relic pods and seams of pyrite, arsenopyrite, sphalerite and galena are found here. Surface weathering has oxidized much of the sulfide minerals, leaving a dark brown goethite stain on the quartz.

Secondary minerals of interest include adamite, zincian symplesite, scorodite, rozenite, copiapite, kornelite, melanterite, woodruffite and gypsum.

Location B represents a small area in a fine-grained limestone which caps the calc-silicate rocks at the western boundary of the quarry. A single small mass of tetrahedrite was discovered here. Except for isolated pods, most of the tetrahedrite has weathered into a mixture of azurite, malachite and stibiconite. The limestone also hosts small weathered specks of chalcopyrite containing covellite.



Figure 2. A view of the Kalkar quarry facing west, showing the fault. May 1960.

Below this zone a large boulder of silica-rich rock was exposed which contained meneghinite veins measuring from 1 to 3 cm in thickness.

Location C was considered to be the most productive mineralized zone of the quarry. This area was a constant source of meneghinite, jamesonite and boulangerite. A silica-rich bench exists here which contains abundant arsenopyrite in crystals associated with deep red kermesite. The kermesite has originated from thin films of stibnite along the fracture surfaces of the silica-rich rock. In addition to a number of common minerals, isolated finds of dravite in fine, brown, striated crystals and green sprays were recovered. In the pure masses of quartz, which contained the brown dravite, small prismatic crystals of stibnite were common. The meneghinite at this location rarely contained clear to light yellow grains of cassiterite. Also at this area a single crystal of allanite was recovered in a quartz-rich calc-silicate rock (this was the only occurrence of a rare-earth-bearing mineral in the quarry). Small masses of cobaltian loellingite with arsenopyrite were also found in this area.

Locality D represents the probable location of the large masses of franckeite with native bismuth and stannite found during collecting in the 1940s and earlier. Also from this area masses of pyrrhotite containing anhedral grains of fluorapatite were found. It is most probable that the single sample of graphitic limestone containing minute grains of stannite, tetrahedrite and uraninite came from this area. Most of the rock now filling this area is waste rock from other portions of the quarry.

Location E is the general area where the two faults intersect. Although now covered with fill, some very unusual rocks were encountered during early operations. Communications with Fred Johnson revealed that some of the rock quarried here had been

dumped in a pile a short distance from the fault intersection. This dump area, which measured no more than 5 by 10 meters, contained a number of old boulders probably quarried during the 1930s. They were discovered partially buried among several willow trees and were generally composed of calc-silicates with veins of quartz and tremolite. During night exploration of this area, using a shortwave ultraviolet light, abundant red fluorescent calcite was found together with a blue-white fluorescent mineral which later proved to be the new mineral pabstite, the tin analog of benitoite (Gross et al., 1965). Small crystals of celsian, galena and massive witherite were also discovered with the pabstite. The rock containing the pabstite also contained large cleavage sections of a darkbrown mineral admixed with tremolite fibers. X-ray methods proved this mineral to be titantaramellite (Alfors and Pabst, 1984). This locality so far has produced the largest specimens of titantaramellite ever found.

One of the most interesting finds was made in the fault zone of the northwest-trending fault at location F. Here, major quantities of high-temperature rocks containing forsterite and diopside with titanite and sulfides occurred. A large mass of rock, broken by blasing, contained fractures coated with a green mineral. This coating was found to be bright apple-green crystals of magnesian annabergite, the first mineral containing nickel to be found in the quarry. Also present were minute, clear, glassy crystals of hoernesite attached to secondary calcite crystals. The matrix rock was later found to contain narrow veins of a bright silvery mineral together with a blue-black mineral that resembled graphite. Abundant black sphalerite was also present which contained very thin yellow-orange coatings of greenockite. The silvery mineral and the blue-black mineral were later identified as gersdorffite and molyb-

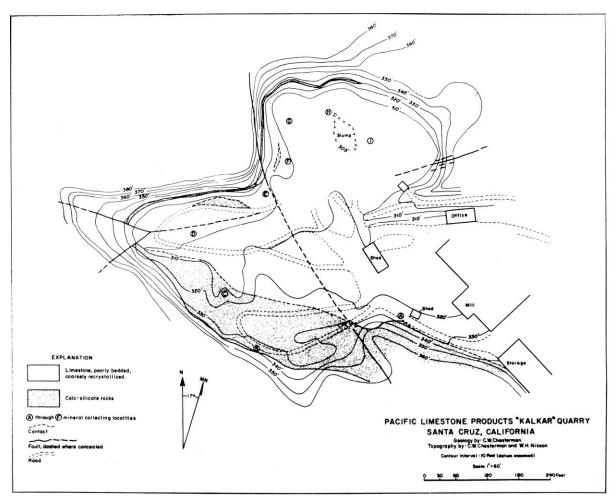


Figure 3. Map of the Kalkar quarry (from Gross et al., 1967).

denite respectively. At this same locality a small cavity was found which contained small but well-developed crystals of amethyst covered by small secondary calcite crystals.

The sulfide-bearing diopside-forsterite rock had been fractured, followed by carbonate cementing. When freshly broken, these seams contain small cavities containing a number of secondary minerals including arseniosiderite, aragonite, calcite, huntite, powellite and wulfenite. The powellite occurs as minute "roses" covering secondary calcite. Anhedral grains of wulfenite were found embedded in massive calcite associated with amesite.

Location G was composed mainly of large blocks of limestone. The zones between these blocks frequently contained pulverulent masses of calcite, goethite, quartz, pyrolusite and the uncommon mineral coronadite.

Locations H and I contained mostly calcite crystals, talc containing pyrite crystals, antigorite, tremolite and amesite.

A visit to the Kalkar quarry in 1978 found the area overgrown with small willow trees and brush, and the quarry floor covered in many areas by water. The quarry bench at location C was located and several specimens of meneghinite, arsenopyrite and kermesite were collected. Also a few samples of galena were discovered in float boulders which later were found to contain pabstite. The

small pyrite-arsenopyrite-sphalerite vein at location A was also found but it was occupied by a swarm of very angry bees.

In 1983 construction began on a series of private residences which currently cover most of the quarry floor in addition to the surrounding cliffs. The site is now on private land and collecting is not possible. It is regrettable that this most interesting quarry will never produce minerals again.

Had it not been for the keen interest and cooperation of the owner, the late Fred W. Johnson, very few of the rare and unusual minerals would have been found and preserved. Because of his interest in the quarry and its mineral content, two nearly complete collections of Kalkar minerals exist today in the authors' personal collections.

#### **GEOLOGY**

The regional geology of the Santa Cruz quadrangle has been described by Branner *et al.* (1909) and Taliaferro (1943). Hubbard (1943) has briefly summarized their work. More recently, Leo (1967) has examined the plutonic and metamorphic rocks of Ben Lomond Mountain, which is located just to the north of Santa Cruz.

The region consists primarily of Tertiary (Miocene) marine sand-

Table 1. Mineral assemblages at nine locations within the Kalkar quarry (see map).

A	В	C	D	E	F	G
Adamite	Azurite	Actinolite	Bismuth	Boulangerite	Annabergite	Calcite
Arsenopyrite	Bindheimite	Allanite	Chalcopyrite	Calcite	Aragonite	Coronadite
Copiopite	Chalcopyrite	Andradite	Fluorapatite	Celsian	Arseniosiderite	Diopside
Galena	Covellite	Arsenopyrite	Franckeite	Epsomite	Barite	Epsomite
Goethite	Malachite	Bindheimite	Graphite	Galena	Bindheimite	Forsterite
Greenockite	Meneghinite	Biotite	Malachite	Gypsum	Brucite	Pyrolusite
Gypsum	Sphalerite	Boulangerite	Meneghinite	Muscovite	Calcite	Pyrite
Kornelite	Stibiconite	Cassiterite	Pyrite	Pabstite	Clinochlore	Sphalerite
Melanterite	Tetrahedrite	Cerussite	Pyrrhotite	Pyrite	Diopside	Tremolite
Meneghinite		Chalcopyrite	Sphalerite	Sphalerite	Forsterite	Talc
Pyrite		Covellite	Stannite	Titantaramellite	Galena	
Pyrolusite		Dravite	Tetrahedrite	Witherite	Gersdorffite	Н
Rozenite		Franckeite	Uraninite	e no ser en en en eile	Greenockite	Amesite
Scorodite		Galena			Hoernesite	Antigorite
Sphalerite		Graphite			Huntite	Calcite
Symplesite		Jamesonite			Jamesonite	Pyrite
Woodruffite		Kermesite			Meneghinite	Sphalerite
		Loellingite			Molybdenite	Talc
		Malachite			Pabstite	Tremolite
		Meneghinite			Phlogophite	
		Pyrite			Powellite	I
		Pyrrhotite			Pyrrhotite	Amesite
		Stibiconite			Quartz	Antigorite
		Stibnite			Sphalerite	Calcite
		Talc			Titanite	Pyrite
					Tremolite	Talc
					Wulfenite	Tremolite

stones and diatomaceous shales. Quaternary sands, gravels and clays predominate along the southern part of the quadrangle. To the north of Santa Cruz, Ben Lomond Mountain, at an elevation of 600 meters, presents a steep escarpment to the northeast and a long gentle slope on the southwest to the ocean. This mountain is an upward-tilted granite block with a quartz diorite core. Relatively small volumes of metamorphic schist, marble and limestone have been identified in this block.

The sedimentary formations of the region have been heavily folded, crushed and broken, with abundant faulting including the effects of the famous San Andreas fault. Rocks of the Jurassic Franciscan complex predominate in the eastern part of the quadrangle.

Locally, the Kalkar quarry explores a poorly bedded recrystallized limestone containing lens-like strata of calc-silicate rocks which probably belong to the Sur Series (?) of pre-Cretaceous age (Fitch, 1931). These strata range in thickness from less than a meter to about 10 meters. They are generally white in color, but zones of light to dark gray limestone and siltstone are common.

Lenticular, interbedded layers of calc-silicate rock are most conspicuous in the southwestern part of the quarry where their thickness ranges from about 2 meters to 10 meters. One such body, though faulted, is exposed also in the northern wall of the quarry where it gradually pinches out towards the east.

The fine-grained, greenish gray to gray calc-silicate rock is moderately dense, and shows an indistinct foliation. The more massive, medium-green siliceous layers show an abrupt textural change with the fine-grained calc-silicate rocks. These siliceous beds are less conspicuous in the quarry because their dull gray to white color resembles that of the recrystallized limestone beds. The siliceous rock types consist principally of calcite and quartz with

lesser amounts of tremolite, actinolite and diopside. The finegrained schistose rocks are composed mainly of phlogophite mica, calcite and other silicates and show banding and minor foliation. The size of calcite crystals in the recrystallized limestone ranges from several mm to about 3 cm. Hydrogen sulfide is common in the limestone and is characterized by a fetid odor when the rock is freshly broken.

No granitic rocks were observed in the main quarry, but in the smaller quarry, about 200 meters to the south, a narrow dike of altered, coarse-grained quartz diorite occurs in fault contact with coarse-grained, white, recrystallized limestone. No evidence of contact metamorphism was observed there. Crawford (1894) records a glaucophane schist interstratified with limestone in this quarry but at present it is covered by quarry rubble.

Faulting is apparent in the limestone body exposed in the northern quarry. Visible fault surfaces and shear zones are exposed along the massive blocks of limestone. No other local deformation has occurred. The limestone body has a very gentle dip to the east and a low strike. Two fault zones, aligned northwest and northeast respectively, have shear zones from 1 to 4 meters wide and prominent vertical fault surfaces. Field evidence indicates that these faults controlled the mineralization in the quarry.

#### MINERALOGY

The mineral assemblage at the Kalkar quarry is composed of silicate gangue minerals related to contact metamorphism of the limestone and siliceous beds, and a group of sulfides, arsenides and sulfosalts which are the result of metasomatism of the recrystallized limestone. Near-surface weathering of these sulfides, arsenides and sulfosalts has resulted in a suite of secondary minerals which include oxides, carbonates, sulfates, arsenates and molybdates.

#### Native Elements

#### Bismuth Bi

Samples of a fine-grained graphitic limestone from the western section of the quarry in the general vicinity of area D (collected by Charles Milton during the 1940s) contained native bismuth associated with meneghinite, pyrite, and rare crystals of stannite (Gross et al., 1967). No further samples containing native bismuth have been found since that time.

#### Graphite C

Graphite is widespread throughout the recrystallized limestone beds as either parallel layers composed of minute flakes or as foliated masses several cm in size. The minute graphite flakes show a typical hexagonal outline.

#### Sulfides and Arsenides

The ten sulfides and arsenides comprise the largest metallic mineral assemblage in the quarry. Although many of the sulfides found in the quarry are considered common in nature, several are quite rare. The weathering of this mineral group has resulted in a number of secondary minerals.



Figure 4. Arsenopyrite crystal, 5 mm, in quartz. G. Dunning specimen and photo.

#### Arsenopyrite FeAsS

Arsenopyrite, like pyrite, is a major constituent of the recrystallized limestone and of the calc-silicate rocks in the western part of the quarry. Crystals up to 5 cm in length have been found in palecolored limestone, but smaller crystals are more common. These crystals are often intergrown and have a brilliant silver color.

### Chalcopyrite CuFeS<sub>2</sub> Covellite CuS

Copper minerals are rare at Kalkar. Chalcopyrite has been found only as small grains and seams associated with pyrite in white recrystallized limestone and massive quartz near location C. It is commonly altered to a mixture of azurite, malachite and goethite. Covellite is very rare and occurs as thin coatings on fracture surfaces in chalcopyrite from which it was derived. It was identified in polished sections of chalcopyrite (Gross *et al.*, 1967).

#### Galena PbS

Coarsely crystalline masses of galena occur in fine-grained, weathered, calc-silicate rocks removed during early quarry operations and deposited in the western part of the quarry. Galena is commonly associated with tremolite, quartz, titanian pabstite, celsian and titantaramellite. It has been found to be a good field indicator of rocks containing pabstite. Galena has also been identified in place at location A, associated with quartz, pyrite, sphalerite, arsenopyrite and greenockite.

#### Loellingite (Fe,Co)As,

Rare masses of cobaltian loellingite, closely associated with coarsely crystalline arsenopyrite, occur in the calc-silicate rocks along a bench face in the western part of the quarry near location C (Gross *et al.*, 1967). The mineral is indistinguishable from arsenopyrite except by X-ray or chemical analysis.

## **Molybdenite** MoS<sub>2</sub> **Gersdorffite** (Ni,Fe,Co)AsS

Both molybdenite and gersdorffite occur intimately associated with sphalerite in a dense calc-silicate rock along the shear zone of the northwest-trending fault at location F. The molybdenite occurs as minute flakes and masses composing parallel bands in the complex rock. It resembles graphite but is somewhat bluer in color.

Anhedral grains of gersdorffite associated with molybdenite compose veins in the complex calc-silicate rock. Subsequent alteration along fracture surfaces has resulted in coatings and crystals of magnesian annabergite and hoernesite.

#### Pyrite FeS,

Pyrite, one of the commonest sulfide minerals in the quarry, is found in all the rock types. Well-formed crystals showing cubic, octahedral, and pyritohedral forms have been found in the recrystallized white limestone and in masses of pure white talc. Also, vein-like masses of pyrite occur traversing siliceous rock types associated with the sulfosalt minerals.

#### Pyrrhotite $Fe_{1-x}S$

Pyrrhotite, although not as common as pyrite or arsenopyrite, occurs mainly in the calc-silicate rocks in small masses associated with pyrite and sphalerite. Some of the larger masses, measuring up to 5 cm, contain pale yellow anhedral grains of fluorapatite, identified by X-ray powder diffraction and spectrographic methods (Gross *et al.*, 1967).

#### Sphalerite ZnS Greenockite Cds

Dark brown to black vein fillings of massive sphalerite occur in the fine-grained dark limestone, and also as small, discrete crystals associated with pyrite and arsenopyrite in coarse-grained white limestone. Spectrographic analysis of the brown sphalerite indicates a trace of cadmium and iron, whereas analysis of the black sphalerite shows a greater amount of cadmium (up to 1%) and a percent or more of iron.

The black massive sphalerite occurring just north of the fault intersection at locality F contains rare yellow-orange coatings of greenockite. Greenockite has also been identified at locality A in massive quartz containing pyrite, arsenopyrite, galena and sphalerite.

#### Stannite CuFeSnS<sub>4</sub>

Rare crystals of stannite embedded in pyrite and associated with meneghinite and native bismuth were collected during the 1940s by Charles Milton of the U.S.G.S. in the rich metallic zone of the western section. This is the only recorded find of this rare mineral (Gross *et al.*, 1967). A specimen provided the authors by the late Fred W. Johnson, owner of the quarry, was examined by scanning electron microscopy (SEM) and found to contain massive pyrite, stannite, chalcopyrite, galena and tetrahedrite in a graphitic seam in dark gray limestone.

#### Stibnite Sb<sub>2</sub>S<sub>3</sub> Kermesite Sb<sub>2</sub>S<sub>2</sub>O

Poorly formed prismatic crystals, minute grains and films of stibnite occur in quartz-rich rocks in the western part of the quarry associated with meneghinite and arsenopyrite. Stibnite is nowhere

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abundant at Kalkar. Partial alteration of stibnite has resulted in thin films of reddish kermesite along fractures in the quartz. Further alteration to stibiconite is rare and occurs generally as pale yellow to white halos at the ends of the kermesite films.

#### Sulfosalts

Only five sulfosalts have been identified in the limestone beds of the quarry. Of these five, the rare sulfosalts franckeite and meneghinite were found to be the most abundant whereas tetrahedrite is quite rare.

#### Boulangerite Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>

Boulangerite is difficult to recognize in the field because of its close resemblance to meneghinite. It usually has a more fibrous habit when not found associated with either meneghinite or jamesonite. Positive identification requires X-ray analysis.



Figure 5. Franckeite in limestone, 5 cm across, showing platy habit and fine twinning. G. Dunning specimen and photo.

#### Franckeite Pb<sub>5</sub>Sn<sub>3</sub>Sb<sub>2</sub>S<sub>14</sub>

Although now very difficult to find, franckeite was quite common in the western part of the quarry during early quarry operations. Excellent samples of crystals showing the typical, thin, warped and striated habit were recovered from graphitic limestone associated with pyrite. Euhedral, tabular crystals commonly measure up to 6 cm in size. In recent years small amounts of franckeite have been found in a medium gray limestone on a bench in the southwest part of the quarry at location C.

#### Jamesonite Pb<sub>4</sub>FeSb<sub>6</sub>S<sub>14</sub>

Jamesonite is common in the mineralized zones as fresh and partially altered coarsely crystalline masses. Where partially altered it has a distinctive yellow coating of bindheimite and occasional small crystals of cerussite. Close association with both meneghinite and boulangerite is common.

#### Meneghinite CuPb<sub>13</sub>Sb<sub>7</sub>S<sub>23</sub>

Meneghinite, admixed with boulangerite and jamesonite, is the most abundant sulfosalt at Kalkar. It occurs as coarsely crystalline to semi-fibrous masses and isolated pods filling fractures in the calc-silicate rocks in the western part of the quarry, especially at location C. These masses often show polysynthetic twinning resulting in a banded effect. Surface oxidation of meneghinite usually produces a bluish color along cleavage planes.

#### Tetrahedrite (Cu,Fe)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>

Tetrahedrite is quite rare in the limestone of the quarry. One small mass, which measured about 4 cm in maximum size, was dis-

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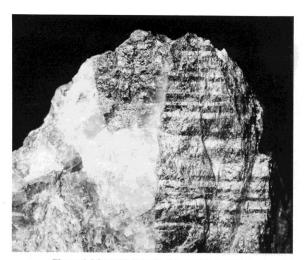


Figure 6. Meneghinite vein, 4 cm, showing twinning. G. Dunning specimen and photo.

covered at location B in the western part of the quarry. It occurred in calc-silicate rock associated with a quartz seam and was partially altered to azurite, malachite and stibiconite. A few minute grains of tetrahedrite were also identified in an old specimen from the western section associated with stannite, pyrite, chalcopyrite and galena.

#### Oxides and Hydroxides

The oxides and hydroxides identified at Kalkar represent an interesting assemblage. The majority of oxide minerals have resulted from oxidation of either sulfides or sulfosalts. A few are the result of metasomatic action during mineralization.

#### Bindheimite Pb<sub>2</sub>Sb<sub>2</sub>O<sub>6</sub>(O,OH)

Bindheimite occurs as the principal oxidation product of jamesonite, boulangerite and meneghinite. It is generally pale yellow in color and is found coating fracture surfaces and masses of the leadbearing sulfosalts.

#### Brucite Mg(OH)<sub>2</sub>

Brucite is a minor constituent along with diopside and forsterite in a thin layer of recrystallized limestone between more massive layers of calc-silicate rocks. It is white and occurs in rounded anhedral grains which are visible only under the petrographic microscope (Gross *et al.*, 1967).

#### Cassiterite SnO

A few very small, honey-yellow, anhedral grains of cassiterite were found embedded in a mass of meneghinite at Location C. The identity was confirmed by X-ray powder diffraction. Cassiterite has also been found associated with titantaramellite and titanian pabstite in siliceous limestone removed from the fault zone many years ago.

#### Coronadite Pb(Mn<sup>+4</sup>,Mn<sup>+2</sup>)<sub>8</sub>O<sub>16</sub>

A dark brown, pulverulent material collected from between large blocks of limestone near locality G was examined in the SEM using energy dispersive spectrometry. A black botryoidal material containing both lead and manganese was identified along with a manganese oxide and quartz. A subsequent X-ray powder pattern gave diagnostic lines for both coronadite and pyrolusite. Abundant goethite comprised the remainder of the material.

#### Goethite $\alpha$ -FeO(OH)

Hydrated iron oxides, which have resulted from the weathering of pyrite and arsenopyrite, have generally been referred to as goethite. It is very abundant at location A and occurs commonly as shiny, dark brown botryoidal coatings.

#### Pyrolusite MnO<sub>2</sub>

Pyrolusite has been identified as dendritic growths on fracture surfaces in limestone throughout the quarry. It is nowhere abundant in any quantity. Powder diffraction patterns of several black managese oxides collected from the quarry gave strong lines for pyrolusite.

#### Stibiconite Sb<sup>+3</sup>Sb<sup>+5</sup>O<sub>6</sub>(OH)

Stibiconite was identified by powder methods as pale yellow to white coatings in fractured quartz, where it occurs as the latest-formed oxidation product of stibnite (formed following kermesite). The pale yellow massive material surrounding a single tetrahedrite sample from location B has been identified as stibiconite.

#### Uraninite UO

Minute dodecahedrons of uraninite were identified as a constituent of a thin graphite seam in limestone associated with pyrite, stannite, galena, chalcopyrite and tetrahedrite. Insufficient material was available for an X-ray powder pattern. An energy dispersive spectrum gave a value for uranium very near that for uraninite.

#### Woodruffite $(Zn,Mn^{+2})Mn_3^{+4}O_7 \cdot 1 - 2H_2O$

An initial SEM examination (by energy dispersive spectrometry) of a brilliant, black, botryoidal mineral coating scorodite crystals revealed the presence of both zinc and manganese. Values of 13.5 % ZnO and 72.0 % MnO were calculated from the EDS spectrum using zinc and manganese oxide standards. A subsequent X-ray powder pattern resembling that of todorokite was obtained.

#### Carbonates

Aside from calcite and aragonite, the carbonates constitute a small fraction of the minerals in the quarry. The abundant groundwater and the humid weather at the quarry (in close proximity to the ocean) have resulted in conditions unfavorable to secondary carbonate formation.

#### Aragonite CaCO<sub>3</sub>

Radiating crystals of aragonite occur along fracture surfaces in limestone in the western part of the quarry. This aragonite fluoresces a bright green under shortwave ultraviolet light. At locality F aragonite occurs with minute crystals of hoernesite along a thin fracture surface.

#### Azurite $Cu_3(CO_3)_2(OH)_2$ Malachite $Cu_2(CO_3)(OH)_2$

Deep azure-blue crystals of azurite associated with green coatings of malachite occur in the western part of the quarry at location B; they formed as a result of the oxidation of tetrahedrite and chalcopyrite. The crystals are small, less than 2 mm long, and are confined to cavities in oxidized tetrahedrite.

#### Calcite CaCO<sub>3</sub>

In addition to massive calcite, which is the main constituent of the recrystallized limestone, good crystals of secondary calcite occur closely associated with the rocks along the fault zones. The rhombohedral form predominates in the western part of the quarry in a small solution cave. In the eastern area of the quarry the scaleohedron form occurs in solution cavities and fractures in the blocky limestone. Pseudocubic rhombohedral forms are abundant along the shear wall of the northwest-trending fault. Fine "nailhead spar" crystals were collected along the northeast-trending fault zone

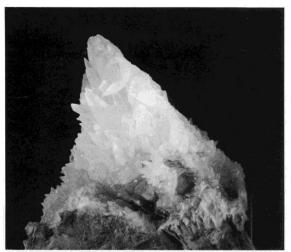


Figure 7. Calcite scalenohedron group on limestone, 9 cm. J. F. Cooper specimen, G. Dunning photo.

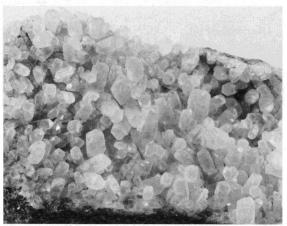


Figure 8. Hexagonal calcite prisms on matrix, 10 cm. J. F. Cooper specimen, G. Dunning photo.

in association with amethyst crystals. These "nailhead spar" crystals are typical hexagonal prisms with rhombohedral terminations. Calcite, showing a vivid red fluorescence, occurs associated with veins of brown sphalerite.

#### Cerussite PbCO<sub>3</sub>

Brilliant, glassy crystals of cerussite associated with bindheimite have been found in cavities in galena and jamesonite at location C.

#### Huntite CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub>

Small white spheroids composed of minute, acicular crystals of huntite occur coating secondary calcite and barite associated with aragonite and magnesian annabergite at locality F. The huntite was identified by X-ray powder diffraction.

#### Witherite BaCO<sub>3</sub>

Witherite is exceedingly rare at Kalkar and was found very closely associated with titanian pabstite, tremolite, quartz and galena (Gross *et al.*, 1967) with a medium-grained siliceous limestone.



Figure 9. Cerussite crystals to 1 mm with bindheimite in jamesonite vug. G. Dunning specimen and photo.

#### Sulfates

Like the carbonates, the sulfates constitute only a small fraction of the mineral content of the quarry. Only during periods of extreme dryness do sulfates others than gypsum and barite form.

#### Barite BaSO<sub>4</sub>

Minute crystals of barite occur sparingly along fracture surfaces at location F, associated with secondary calcite, aragonite, magnesian annabergite and huntite. Abundant sepiolite also occurs along these fractures.

#### Epsomite $MgSO_4 \cdot 7H_2O$

Epsomite is found sparingly, and only during periods of extreme dryness, as light encrustations on fractures in magnesium-rich rocks.

#### Gypsum CaSO<sub>4</sub> • 2H<sub>2</sub>O

Gypsum is very common throughout the quarry and occurs along fractures in the pyrite-bearing calc-silicate rocks. It is especially abundant at location A.

Melanterite  $FeSO_4 \cdot 7H_2O$ Kornelite  $Fe_2(SO_4)_3 \cdot 7H_2O$ 

Copiapite Fe<sup>+2</sup>Fe<sub>+</sub><sup>+3</sup>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> •20H<sub>2</sub>O

These three iron sulfates occur as efflorescences on fracture surfaces of pyrite-arsenopyrite-sphalerite veins at location A. They only occur during periods of extreme dryness.

#### Rozenite FeSO<sub>4</sub> • 4H<sub>2</sub>O

This rare sulfate occurs as a white powder (which is quite delicate) on fractures in broken and sheared siliceous rocks at location A. It was identified by X-ray diffraction and is the second occurrence reported for this mineral in California (Gross *et al.*, 1967).

#### Phosphates, Arsenates and Molybdates

Except for fluorapatite, the members of these groups have resulted from the oxidation of sulfides of iron, zinc, molybdenium or nickel. Their occurrence is limited to those mineralized areas rich in corresponding sulfides and arsenides.

#### Adamite Zn<sub>2</sub>(AsO<sub>4</sub>)(OH)

Adamite, associated with scorodite and goethite, occurs as color-

less, transparent bow-tie groups of rounded crystals filling alteration cavities that host a number of secondary minerals at location A. These adamite groups are weakly fluorescent pale green under shortwave ultraviolet light.



Figure 10. Magnesian annabergite crystals to 0.15 mm. G. Dunning specimen and SEM photo.

#### Annabergite (Ni,Mg)<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

Small, pale apple-green crystals of magnesian annabergite coat fracture surfaces in the gersdorffite-molybdenite-sphalerite vein of calc-silicate rocks at location F. The monoclinic crystals are acicular [001] and flattened on {010}. Crystals form spheroidal groups with the crystal terminations forming the outer surface of the spheroid. Identification was confirmed by X-ray diffraction and spectrographic analysis. Secondary calcite has been found covering many of the magnesian annabergite groups.

#### Arseniosiderite Ca<sub>3</sub>Fe<sub>4</sub>(AsO<sub>4</sub>)<sub>4</sub>(OH)<sub>6</sub>•3H<sub>2</sub>O

Reddish-brown botryoidal coatings of arseniosiderite occur as an oxidation product of arsenopyrite along fracture surfaces at location F. Only two small samples have been recovered from the locality. The mineral occurs closely associated with minute acicular aragonite crystals and zincian nepouite. Identification was made by X-ray diffraction and energy dispersive spectrometry.

#### Fluorapatite Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F

Fluorapatite is the only phosphate mineral identified in the limestone body at Kalkar. It is quite rare and only a few specimens are known. The only preserved specimens are composed of pale yellow anhedral grains forming small masses in massive pyrrhotite. Its identification was established by X-ray diffraction and chemical analysis (Gross *et al.*, 1967).

#### Hoernesite Mg<sub>3</sub>(AsO<sub>4</sub>) • 8H<sub>2</sub>O

Minute, clear prismatic crystals of hoernesite associated with aragonite occur as fracture fillings at location F. The crystals show sharp monoclinic terminations and are usually found as small groups of divergent crystals. The mineral was identified by X-ray diffraction and spectrographic analysis.

#### Powellite CaMoO<sub>4</sub>

Minute, dull white crystal aggregates of powellite occur on corroded faces of secondary calcite associated with magnesian annabergite at location F. The individual crystals show a creamy yellow to golden yellow fluorescence under shortwave ultraviolet light. The mineral is very rare and has resulted from the oxidation of

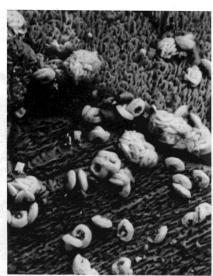


Figure 11. Crystals of powellite to 12 microns on calcite. G. Dunning specimen and SEM photo.

minute molybdenite flakes in the hard calc-silicate rock. Identification was made by energy dispersive spectrometry.

#### Scorodite Fe(AsO<sub>4</sub>) • 2H<sub>2</sub>O

Scorodite occurs as one of the alteration products of the pyritearsenopyrite-sphalerite veins at location A. It generally forms minute pyramidal orthorhombic crystals with a light green color, coating fracture surfaces and cavities of the oxidized sulfide-quartz vein.

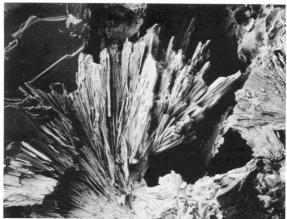


Figure 12. Indigo-blue, zincian symplesite spray, 1 mm. G. Dunning specimen and SEM photo.

#### Symplesite $(Fe,Zn)_3(AsO_4)_2 \cdot 8H_2O$

Deep indigo-blue crystals and coatings of zincian symplesite, showing a coarsely fibrous radial habit, occur in the highly oxidized portion of the sphalerite-arsenopyrite-pyrite vein at location A. It is closely associated with gypsum, scorodite and goethite along fractures in the vein rock. The mineral was identified by X-ray diffraction and energy dispersive spectrometry.

#### Wulfenite PbMoO.

Minute, yellow-orange, anhedral crystals of wulfenite occur embedded in silica and calcite along fracture surfaces at location F. The source of the lead is believed to have been galena, although none has been identified at this locality. The identification of the wulfenite was made by energy dispersive spectrometry.

#### Silicates

The silicates constitute the largest group of minerals found at Kalkar. They are generally the product of contact metamorphism of silica beds associated with limestone, and of metasomatic action along the fault system of the quarry.

#### Actinolite Ca<sub>2</sub>(Mg,Fe)<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>

Dark green elongated crystals and masses of actinolite, associated with tremolite, occur in the quartz-rich sulfide-bearing veins of the west quarry contact area. It is the main silicate of the boulangerite-meneghinite-jamesonite sulfosalt assemblage.

Allanite (Ca,Ce,Al)<sub>2</sub>(Fe<sup>+2</sup>,Mg)(Al,Fe<sup>+3</sup>)<sub>2</sub>O•(Si<sub>2</sub>O<sub>7</sub>)(SiO<sub>4</sub>)(OH)
Allanite is very rare in the calc-silicate rocks at Kalkar. A single dark brown crystal, showing four faces, was found at location C. It was identified by X-ray diffraction; energy dispersive spectrometry indicates equal amounts of Ce and La in the crystal.

#### Amesite Mg<sub>2</sub>Al(Si,Al)O<sub>5</sub>(OH)<sub>4</sub>

Pale green crystals of amesite occur embedded in talc in the north part of the quarry at location H.

#### Andradite Ca<sub>3</sub>Fe<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

Several small andradite crystals, less than 2 mm in size, were recovered from the contact metamorphic zone at location C. They were embedded in a fine-grained limestone. They are dark brown in color and show the dodecahedral form.

#### Antigorite (Mg,Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>

Pale greenish antigorite forms part of the alteration of forsterite in the calc-silicate rocks at location F.

#### Biotite K(Mg,Fe)<sub>3</sub>(Al,Fe)Si<sub>3</sub>O<sub>10</sub>(OH,F)<sub>2</sub>

A few rare flakes of biotite were found in the calc-silicate rocks that contained an abundance of arsenopyrite and pyrite. Biotite also was observed with feldspar in the quartz diorite block of the small quarry to the south.

#### Celsian BaAl, Si, O,

Celsian is very rare at Kalkar. Small crystals less than 3 mm in length occur in tremolite with titantaramellite and titanian pabstite. It also occurs as vein fillings in phlogopite schist and can be recognized by its cleavage and pale gray color. It was identified by X-ray powder diffraction.

#### Chondrodite $(Mg,Fe)_5(SiO_4)_2(F,OH)_2$

Small anhedral crystals of chondrodite occur sparingly in the recrystallized limestone near the quarry faults. Its color is usually dark golden brown (Leo, 1967).

#### Clinochlore (Mg,Fe)<sub>5</sub>Al(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>8</sub>

A chlorite mica near clinochlore in composition occurs as pale green foliated masses associated with phlogopite and pyrite in the calc-silicate rocks in the western quarry section.

#### Diopside CaMgSi<sub>2</sub>O<sub>6</sub> Forsterite (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>

Both diopside and forsterite occur as colorless, xenoblastic grains in the recrystallized limestone. The forsterite is altered in part to pale greenish antigorite and white to pale green talc (Gross *et al.*, 1967).

#### Dravite NaMg<sub>3</sub>Al<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>

Rare prismatic crystals of green dravite were found in the western part of the quarry embedded in a graphitic limestone. The crystals show a radiating habit parallel to the graphite seam. In the same general area several small prismatic brown crystals of dravite were found in quartz-limestone rock associated with stibnite. Both samples were identified by X-ray powder diffraction and energy dispersive spectrometry.

#### Meionite 3CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> • CaCO<sub>3</sub>

Meionite has been observed sparingly in the impure marble, associated with diopside (Leo, 1967).

#### Muscovite KAl<sub>2</sub>(Si<sub>3</sub>Al)O<sub>19</sub>(OH,F)<sub>2</sub>

Muscovite occurs rarely in the calc-silicate rocks. It was observed associated with boulangerite in the western part of the quarry.

#### Nepouite (Ni,Zn)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)

Nepouite rich in zinc occurs as yellowish green spheroidal coatings covering aragonite and calcite along fracture surfaces at location F. It is closely associated with arseniosiderite. The mineral was identified by X-ray diffraction and energy dispersive spectrometry.

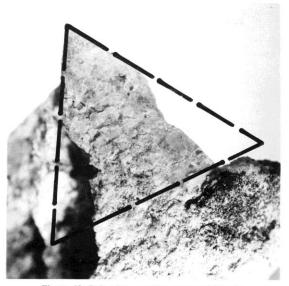


Figure 13. Pale pink, partial crystal of titanian pabstite, 3.5 cm, showing trigonal symmetry. J. F. Cooper specimen, G. Dunning photo.

#### Pabstite Ba(Sn,Ti)Si<sub>3</sub>O<sub>9</sub>

The new mineral pabstite was discovered in 1963 (by the authors) in recrystallized siliceous limestone, and subsequently described by Gross *et al.* in 1965. Pabstite occurs as anhedral grains and masses which are colorless to white with a pink tinge when freshly broken. It is also found very rarely in partial crystals with a trigonal outline. Field identification is very difficult except when searching with a shortwave ultraviolet light which reveals a bluish white fluorescence.

Pabstite is found in close association with titantaramellite, witherite, galena, cassiterite and sphalerite. Both galena and sphalerite, when found together, are good field indicators for pabstite.

#### Phlogopite KMg<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH,F)<sub>2</sub>

Abundant phlogopite mica occurs as pale pinkish brown to colorless plates in the calc-silicate rocks which are interbedded in limestone. This mica is the major component of the mica schists exposed throughout the quarry.

#### Quartz SiO<sub>2</sub>

Massive quartz occurs abundantly throughout the western part of the quarry as a constituent of the calc-silicate rocks. Fine-grained quartz, resembling porcelain, is usually found with tremolite cutting the recrystallized limestone. Amethyst was found at location F as small, pale purple crystals in a fracture in siliceous limestone. Secondary calcite rhombohedrons cover most of the amethyst crystals.

#### Sepiolite Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>•6H<sub>2</sub>O

Sepiolite occurs throughout the recrystallized limestone as thin coatings along fracture surfaces (Leo, 1967).

#### Talc Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>

Talc occurs as small masses of foliated flakes in the calc-silicate-free limestone of the northern section of the quarry. The talc often contains pyrite cubes up to 1 cm on an edge.

#### Titanite CaTiOSiO<sub>4</sub>

Titanite, in xenoblastic, brown grains less than 1 mm in size, is abundant in the calc-silicate rocks of the quarry (Gross et al., 1967).



Figure 14. Anhedral titantaramellite crystal, 10 cm. G. Dunning specimen and photo.

#### **Titantaramellite** $Ba_4(Ti,Fe,V,Mg)_4(B_2Si_8O_{27})O_2Cl_x$

Large, dark brown to black, anhedral crystals of titantaramellite up to 10 cm in size occur in float material removed during quarry operations many years ago. This mineral occurred locally in the contact metamorphic limestone near the fault zones and is usually intergrown with tremolite. Associated minerals include celsian, titanian pabstite, galena, cassiterite and quartz. The titantaramellite from Kalkar contains the highest concentration of vanadium (3.2%  $\rm V_2O_3$ ) of all the titantaramellites analyzed (Alfors and Pabst, 1984). The titantaramellite crystals from this locality are among the largest in the world.

#### Tremolite Ca<sub>2</sub>Mg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH),

Tremolite is one of the most abundant silicate minerals in the quarry. It is most common in the areas adjacent to the faults where it forms slickenside surfaces up to several cm in thickness. Its texture ranges from massive granular to coarse elongated crystals. The variety "mountain leather" is found coating surfaces between fault blocks in the limestone in the northern section of the quarry.

#### **PARAGENESIS**

Only a few of the sulfides found at the Kalkar quarry show sequential relationships. Arsenopyrite has been found included in massive sphalerite which in turn contains small veinlets of chalcopyrite and pyrite. Sulfosalts border the iron sulfides and may fill fractures in non-metallic minerals. A paragenetic sequence for the Kalkar sulfide-sulfosalt mineralization was difficult to formulate because of the spotty nature of the sulfide-sulfosalt occurrences throughout the quarry.

Gross et al. (1967) have concluded, based on limited evidence from polished sections and field relationships, that an overlapping sequence of sulfide formation occurred with molybdenite, cobaltian loellingite and gersdorffite forming earliest at temperatures possible above 600° C. Later, arsenopyrite, chalcopyrite, pyrrhotite, pyrite, and sphalerite formed, perhaps below 555° C. The sulfosalts formed last at temperatures below 400° C.

#### DISCUSSION

The Kalkar quarry differs from other limestone quarries in the Santa Cruz vicinity in the amount and type of impurities in the original sediments and in the degree of metasomatic action that occurred along the transverse faults. These Sur Series (?) limestones generally contain large amounts of silica and iron. Metamorphism by a nearby plutonic body is believed to have formed the forsterite-diopside-phlogopite assemblage and the tremolite-actinolite facies. It is probable that some of the elements were in the existing sediments, most notably Ba, Fe, Zn and Ti, while others, such as Sn, Pb, Sb, As, Mo, Co and Ni, were probably introduced during metasomatic alteration.

Although mineralization at the Kalkar quarry is of limited extent, it is nevertheless unique in mineral content in an area which is dominated by non-mineralized marine deposits. Pabstite, the tin analog of benitoite, has not been discovered at any other locality. In addition to pabstite the quarry has produced some of the largest specimens of franckeite, meneghinite and titantaramellite known in North America.

#### ACKNOWLEDGMENT

The authors wish to acknowledge the interest and cooperation of the late Fred W. Johnson, owner of the Pacific Limestone Products quarry. Through his observations and recollection the authors were able to reconstruct the probable location of many early mineral occurrences; and he generously presented us with several superb samples of franckeite, calcite, malachite and azurite which were preserved from early mining operations.

This paper is dedicated to the late Fred W. Johnson in recognition of his keen interest in quarry mineralogy and specimen preservation.

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