Spurrite from northern Coahuila, Mexico

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Summary. Spurrite-bearing contact-metasomatic mineral assemblages occur with a few of the many rhyolite stocks intrusive into Georgetown (Cretaceous) limestone in the Encantada district of northern Coahuila, Mexico. The contactmetasomatic suites are found associated only with rhyolites that solidified within the thick Georgetown limestone. Rhyolites that penetrated through the limestone have sharp contacts commonly marked by perlitic contact breccias. The structural form of all the rhyolites indicates intrusion under high pressure.

Three distinct contact-mineral suites have been recognized: Foliated garnetwollastonite rocks occur adjacent to the rhyolite, whereas spurrite is only found further from the intrusive. The inner side of the spurrite-bearing zone is characterized by foliated spurrite-garnet-periclase rocks, whereas the outer side of the spurrite zone consists of a massive, coarse-grained, spurrite-rankinite-periclase rock, which has a sharp contact with the outermost foliated marble zone. At one location, massive spurrite occupies 'dikes' radial to the intrusive, which are postdated by wollastonite-bearing gehlenite-diopside rocks.

It is concluded that the stages of rhyolite emplacement include: First, preliminary high-pressure structural site preparation accompanied by intrusion of rhyolite and metasomatic introduction of Si and Al into preheated cap rock. Then crystallization of the metasomatic zone, under conditions of upward pressure exerted by the rhyolite, to give the features of the spurrite zone; followed by conversion of the inner side of the spurrite zone to a wollastonite-bearing assemblage.

SPURRITE, $2Ca_2SiO_4$. CaCO₃, was discovered in the Encantada district of northern Coahuila in 1958 during reconnaissance examination of the contacts of rhyolite plugs intrusive into massive limestone. Although several tens of rhyolites were examined in this area, spurrite has been found only in two localities, namely at Pico Encantada and associated with a group of intrusives termed the Rosa group. In order to determine the reason for this restricted occurrence of the spurrite mineralization, the more detailed examination outlined herein was performed.

Several spurrite occurrences have been previously described, including such classical localities as Scawt Hill, Co. Antrim (e.g., Tilley, 1930), and Crestmore, California (e.g., Eakle, 1927), as well as localities geographically relatively close to Encantada, including Velardeña, Durango, the 842

type locality for spurrite (Spurr and Garrey, 1908), and the Christmas Mountains of Texas (Clabaugh, 1953). In spite of this previous work, it is felt that the Encantada occurrences merit description, as the good rock exposures there yield evidence from which the stages in the emplacement history of the rhyolites can be deduced.

The Encantada district is one of the principal fluorspar producing areas of Mexico. It is readily accessible by gravel road from the town



FIG. 1. Northern Coahuila, showing location of the Encantada district.

of Muzquiz (fig. 1). The district lies on the south end of the Encantada mesa, a spectacularly scenic north-south trending limestone platform with an average elevation of about 5200 ft. The mesa is bounded on the west by the Boquillas Valley graben, which extends north into the Big Bend region of Texas. The south end of the mesa is dominated by a conical hill, Pico Encantada, which rises over 6000 ft.

Geology

The limestones on the Encantada mesa are of Lower Cretaceous age. The principal limestone, the Georgetown, is host rock for all the spurrite occurrences discovered. This formation, over 700 ft thick, is a finegrained, thick-bedded, massive limestone that is uniform in appearance throughout its exposed thickness. The limestone is broadly folded into

asymmetric north-westerly trending folds that are truncated on the west by the Boquillas graben fault system. Superimposed on this broad structure is a complex of faults and joints that cut the Georgetown limestone. A more detailed account of the stratigraphy and structure has been given by Temple and Grogan (1963).

The igneous rocks of the Encantada district are predominantly rhyolites, which occur both as plugs and sills. These intrusives exhibit features common to many of the rhyolites in northern Coahuila; important examples have recently been described from the Pico Etereo district, which lies approximately 50 miles north of Encantada (McAnulty *et al.*, 1963; Daugherty, 1963).

The rhyolite plugs at Encantada can be subdivided on the basis of the nature of the contact with the host limestone. The great majority, over 90 %, are similar in mode of occurrence, internal structure, and petrography. These rhyolites are characterized by a sharp contact with little or no recrystallization of the limestone; perlitic contact breccias with blocks and fragments of olivine basalt are not uncommon. Typically, these rhyolites form prominent topographic features rising several hundred feet above the surrounding limestone. The intrusives are circular in plan, generally less than one-half mile in diameter, and exhibit pronounced internal inward-dipping flow banding that parallels the plug contact. In vertical section, many of the rhyolites have the shape of an inverted cone. Typical structural relationships with the surrounding limestone include local sharp updoming and the development of ring faults with throws of several hundred feet. In the Pico Etereo district to the north, spectacular examples of both 'trapdoor' domes and ring structures are exposed.

The second type of rhyolite body is characterized by a peripheral contact metasomatic aureole, which generally includes both spurrite and garnet rocks as well as recrystallized host limestone. The significant feature of these rhyolites is that they occur below the present topographic level of the top of the Georgetown limestone. They therefore presumably crystallized under a cap of limestone. Typical examples occur in the Rosa group of intrusives, which are located in the topographically low area on the east side of the Encantada mesa. Spurrite also occurs, however, on the topographically prominent Pico Encantada, a pronounced dome of limestone in which the central rhyolite core has been only recently apically exposed by weathering.

Petrographically the two types of rhyolite are distinct. Both types are flow banded. The more abundant crosscutting type is spherulitic with patches of fine- to medium-grained quartz between the bands of spherulites. These rocks also contain phenocrysts of angular quartz and sanidine pieces; accessory minerals include magnetite and apatite. In contrast, the rhyolites with associated spurrite are porphyritic with euhedral phenocrysts of orthoclase and albite in a medium-grained anhedral granular matrix that consists largely of orthoclase with minor quartz and biotite, with accessory magnetite, apatite, and zircon.

CONTACT METASOMATISM

Rosa group

The Rosa group of rhyolite intrusives lies approximately two miles ENE of the prominent Pico Encantada at the south end of the Encantada mesa. The group lies at an average elevation of about 4700 ft, i.e. approximately 500 ft below the east rim of the mesa. The intrusives are visible from the ore road that follows the rim of the mesa and can be reached by foot from this road. The location of the contact metasomatic rocks with respect to the road is shown in fig. 2. Vertical relief within the area of fig. 2 is about 800 ft, and bed rock is exposed over approximately 30 % of the area. A vertical section through the largest metasomatic aureole is given in fig. 3. The intrusive is cone-shaped, and the contact metasomatic rocks cap the cone, with only minor metasomatism along the nearly vertical sides of the intrusive. The true thickness of the silicate-bearing portion of the aureole varies, therefore, from zero to over 100 ft, depending on location with respect to the intrusive.

Within this aureole, the following three zones can be distinguished on the basis of both structural relations as seen in the field and mineralogy:

Garnet-wollastonite zone. This lies immediately adjacent to the rhyolite. It is generally narrow and ranges from a few inches to five feet in thickness where exposed on the sides of the intrusive. Immediately adjacent to the rhyolite the rocks locally are brecciated, whereas in the outer part of the zone a banded texture is typical. This banding parallels the foliation within the rhyolite and dips steeply inwards on the sides of the intrusive.

The rhyolite is altered along the contact with the garnet-wollastonite zone. In the altered zone, which is only a few inches wide, the porphyritic texture of the rhyolite is retained. The altered rock consists of phenocrysts of albite in a matrix of fine-grained orthoclase with inter-

stitial anhedral aegirine. In addition, the rock contains scattered small diopside phenocrysts rimmed by aegirine.

The breccia noted on the inner side of the garnet-wollastonite zone consists of dark brown angular fragments in a lighter coloured matrix.



FIGS. 2 and 3. FIG. 2 (top). Geology of the Rosa group of intrusives, showing the location of section A-A₁ (fig. 3). FIG. 3 (bottom). Vertical section A-A₁ through metasomatic aureole, Rosa group.

In thin section, the darker fragments are seen to consist of dark brown, dirty garnet with interstitial dirty manganiferous calcite and local stubby clear areas, largely occupied by fibrous tremolite and fresh calcite, with a few clear yellow garnets and accessory apatite. The lighter crosscutting rock consists of subhedral light-coloured yellowish garnet with interstitial calcite and apatite and patches of wollastonite, tremolite, and albite with minor cancrinite. The alternating light and dark brown bands of the banded rock on the outer side of the zone correspond in composition to the two phases observed in the breccia. In one sample from close to the rhyolite, the banded rock is in contact with a coarse-grained ijolite (aegirinenepheline rock with sodalite and accessory apatite and sphene). This subsilicic rock has been found only at, or very close to, the contact of the rhyolite; it is rare and constitutes less than 1 % of the indicated volume of the garnet-wollastonite zone.

Spurrite zone. Spurrite occurs in a zone that is separated from the rhyolite by the inner garnet-wollastonite zone and is bounded externally by the outer marble zone. The spurrite zone varies in thickness from a few feet on the vertical flank of the intrusive to over 100 ft on the top of the intrusive. The outer side of the zone is marked by the presence of large spurrite crystals, which range up to six inches in length (fig. 4), although close to the rhyolite the spurrite is finer in grain size. The outer contact with the marble zone is sharp.

The spurrite was identified optically and by X-ray means. The mineral forms well-developed crystals of stubby prismatic habit. It is biaxial negative, 2V about 35° , r > v weak. It shows at least one good cleavage direction and exhibits both single and multiple twinning in two directions with an angle of about 58° between the two twin individuals. In addition, the mineral effervesces with dilute HCl, yielding a gelatinous silica residue.

The foliated fine-grained rocks on the inner side of the zone consist of spurrite, garnet, calcite, and euhedral pseudomorphs of brucite after periclase, with accessory magnetite and apatite. Outwards across the zone, the garnet content decreases, while the number of brown brucite pseudomorphs increases. On the inner side of the zone the subhedral colourless-to-yellow garnet exhibits granular dirty brown cores; on the outer side of the zone the colourless to yellow garnet is homogeneous. Wollastonite has been identified in small quantities in banded spurritebearing rocks only from the inner margin of the spurrite zone.

The outer side of the spurrite zone is marked by the occurrence of massive spurrite. Here the spurrite generally forms a blocky equigranular aggregate but also occurs as bladed radial and spherulitic aggregates. The coarse spurrite is accompanied by minor amounts of a mineral tentatively identified as rankinite (biaxial positive; $2V = 50-60^{\circ}$, moderate relief [less than spurrite], colourless, multi-lamellar twinning). Magnetite is a rare accessory throughout the spurrite zone.

Marble zone. The marble zone lies on the outer side of the silicate



FIGS. 4a and 4b. Fig. 4a (top). Banded spurrite-garnet-periclase rock from the inner margin of the spurrite zone, Rosa group. (Spurrite white.) FIG. 4b (bottom). Massive spurrite rock, outer side of the spurrite zone, Rosa group.

zones described above. It reaches over 1000 ft in outcrop width and is approximately 200 ft in thickness above the top of the rhyolite. The contact with the adjacent spurrite zone is sharp. On the inner side of the zone, the foliation of the marble parallels the foliation of the rhyolite and calc-silicate rocks. However, on the outer side of the zone the Georgetown limestone is locally foliated along joints and bedding planes and thus a relict texture of patches of limestone surrounded by gneissic marble can be seen.

Mineralogically, the marble zone is relatively simple. The inner side is a dark grey rock that consists of a dirty, very strongly twinned and sheared, manganiferous carbonate, and a clear, only slightly twinned variety; the clear type forms metacrysts in the dirty carbonate. In contrast, the marble near the outer edge of the zone consists of large anhedral twinned calcite crystals separated and cut by fine-grained granular anhedral calcite; along the grain boundaries and replacing the calcite are tabular opaque minerals identified by X-ray means as braunite, (Mn,Si)₂O₃, and hausmannite, Mn₃O₄.

Both the marble zone and the surrounding unaltered Georgetown limestone are cut by scattered veinlets of a brown siliceous rock that appears to be spatially related to the rhyolite intrusion. Typically this rock consists of slender prismatic quartz crystals in a subparallel texture. The rock has been observed filling intricate stylolite structures in the limestone. Adjacent to these siliceous stringers the limestone usually contains disseminated slender prismatic quartz crystals.

Pico Encantada

Pico Encantada forms a prominent conical peak that rises approximately 1000 ft above the level of the Encantada mesa. The peak is a dome of Georgetown limestone with quaquaversal dips of $25-30^{\circ}$. A rhyolite stock approximately 350 ft in diameter is exposed at the centre of the dome.

The contact effects of the rhyolite are well displayed in a gully on the east side of the peak. Three distinct contact metasomatic types can be distinguished:

Radial 'dikes' of spurrite. These occur for a distance of up to onequarter of a mile from the rhyolite contact and vary from a few inches to over one foot in thickness. These 'dikes' are truncated by the inner silicate zone described below. In thin section, the massive hard white 'dike' filling is seen to consist largely of a mosaic of fine-grained calcite and serpentine pseudomorphs after spurrite, with scattered small

pseudomorphs of brucite after periclase, and stellate wollastonite crystal aggregates along cracks in the rock. Contacts of the 'dikes' are sharp.

Calc-silicate zone. Approximately 150 ft in width, a foliated green silicate rock that parallels the strike of the concentric foliation of the rhyolite. Near the contact of the rhyolite this rock consists mostly of euhedral to subhedral diopside crystals in a matrix of fine granular gehlenite with interstitial fluorite. On the outer side of the zone, local magnetite pods occur in which granular magnetite has apparently replaced the gehlenite-diopside rock. Clots of yellowish-green garnet are found on the outer side of the calc-silicate zone.

Narrow veins of quartz-fluorite rock. These cut both the calc-silicate zone and the peripheral parts of the rhyolite stock. They parallel the foliation of the calc-silicate rock and the rhyolite. Massive black fluorite, which contains inclusions of fibrous silicate minerals and calcite, has been mined on the outer side of the calc-silicate zone on the northeast flank of Pico Encantada.

The occurrence of quartz-fluorite veins is restricted to the rhyolite and siliceous metasomatic rocks. Coarse-grained crystalline quartz does not occur in the important fluorspar-producing mines, which are located within the Georgetown limestone on the Encantada mesa close to Pico Encantada.

Petrogenesis

Two types of rhyolite have been described from the Encantada district. Contact metasomatic minerals occur only associated with the medium-grained porphyritic orthoclase and albite rhyolites that crystallized under a cap of limestone. It is postulated that the retention of volatiles by the limestone cap resulted in reactions that produced the observed contact metasomatic suites. The spherulitic sanidine rhyolites apparently punched through the limestone, lost their volatiles, and crystallized rapidly.

The structural forms of the rhyolite intrusives include 'trapdoor' domes, radial fractures, and ring faults. These forms all suggest intrusion under considerable pressure. An order of magnitude of this pressure can be approximated by comparison of the geometric shape of Pico Encantada with the size of its rhyolite core. This comparison suggests that upward pressures of up to 17 kilobars could have been operative. Other evidence of pressure is provided by the wide zone of foliated rocks found on the Rosa group; in particular the peculiar relict texture of the marble on the rim of the altered zone suggests the effect of high-pressure gas. However, an anomaly in the picture of high-pressure intrusion is presented by the occurrence of massive spurrite sandwiched between the foliated rocks of the outer marble zone and the inner spurrite and garnet-wollastonite zones. The massive spurrite rock is characterized by large crystals, which in many cases exhibit a radial bladed habit. It is difficult to imagine that this massive spurrite crystallized under considerable pressure, and it is therefore concluded that the crystallization of the calc-silicate minerals post-dated the formation of the marble. Previous field and experimental evidence (for example, as summarized in Turner, 1948) indicates that calc-silicate minerals such as spurrite are characteristic of low-pressure, high-temperature conditions.

The radial fractures at Pico Encantada, the formation of which is attributed to upward pressure, are truncated by the concentric calcsilicate zones thus lending confirmation to a high-pressure phase prior to calc-silicate mineralization.

Mineralogically, the calc-silicate metasomatic zones in the Rosa group vary from the assemblage garnet-wollastonite-diopside (tremolite) on the inner side of the aureole to spurrite-rankinite-periclase on the outer side. This mineralogy suggests that silicon was added throughout the aureole whereas aluminium (found in grossular) was added to the inner side only. A similar bulk compositional variation is confirmed at Pico Encantada by the contrast between the spurrite radial 'dikes' and the inner garnet-diopside rocks. The variation in mineralogy between Pico Encantada and the Rosa group indicates a PT difference that is not unexpected in view of the greater cap rock cover on the Rosa group.

Experimental work on the system wollastonite + calcite \Rightarrow spurrite + CO₂ (Tuttle and Harker, 1957) established a *PT* curve for this reaction. Spurrite was formed on the high-temperature side of the curve, and was found to break down into wollastonite and calcite with decreasing temperature within the CO₂ pressure range investigated (0 to 6000lb in.²).

At first glance, the field evidence is incompatible with these experimental results. Thus the higher temperature phase, spurite+rankinite, is separated from the presumed magmatic heat source by wollastonitebearing rocks, which theoretically form at lower temperatures. Furthermore, the outer spurite-marble contact is sharp at both Pico Encantada and on the Rosa group and there is no intervening wollastonite-bearing zone. These field observations at Encantada are reinforced by the published description of the type locality of spurite at Velardeña, Mexico (Spurr and Garrey, 1908), where the spurite rock is separated from the intrusion by a garnet-silicate zone.

The field evidence can, however, be reconciled with the available experimental data in a manner compatible with a logical sequence of rhyolite intrusion. In the first place, the occurrence of apparently lower-grade rocks at the inner margin of the contact aureole could indicate that even though the temperature was highest at this location, pressure also was higher than in the outer part of the spurrite zone. The occurrence of stubby pseudomorphs of tremolite, etc., after spurrite in the garnet-wollastonite zone indicates that the rocks of this zone are actually a metamorphic replacement of the rocks of the inner side of the spurrite zone. It is concluded therefore that this area must have been subjected to a change in either pressure or temperature or both during its cooling history. It is postulated that the calc-silicate rocks crystallized under the influence of pressure exerted on the inner side of the metasomatic aureole by the rhyolite intrusive.

The sharp contact between spurrite and marble at both Pico Encantada and on the Rosa group can be explained if this contact is regarded as the outward limit of metasomatic introduction of a finite amount of Si into preheated country rock. Preheating presumably was accomplished during the initial high-pressure phase of intrusion. Crystallization of the rocks of the outer part of the metasomatic aureole under conditions of low pressure distant from the upthrusting rhyolite would allow development of coarse-grained spurrite. Increasing pressure closer to the intrusive would influence the formation of finer-grained foliated rocks, and with either a temperature decrease or further pressure increase the PT conditions would eventually move from the stability field of spurrite to that of wollastonite and calcite.

It is concluded that the emplacement history of the Encantada rhyolites is preserved only around those intrusives that did not penetrate through the thick Georgetown limestone. Interpretation of the observed structural and mineralogical features of these rhyolites leads to recognition of three principal stages of intrusion:

Preliminary high-pressure structural site preparation, accompanied by emplacement of rhyolite, formation of marble, heating of country rock, and metasomatic introduction of Si and Al into preheated cap rock. This was followed by crystallization of the metasomatic contact zone, under conditions of pressure exerted by the upthrusting rhyolite, to give the features of the spurrite zone; with continued pressure, or decrease in temperature, or both, the inner side of the spurrite zone was converted to a wollastonite-bearing assemblage; subsilicic rocks locally concentrated at the rhyolite margin crystallized after cessation of the upward pressure. Thirdly, there was a late-stage fluorite mineralization.

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