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THERMAL EFFECTS OF LARGE BODIES OF INTRUSIVE SERPENTINITE ON OVERLYING MONTEREY SHALE, SOUTHERN DIABLO RANGE, CHOLAME AREA, CALIFORNIA

By K. J. MURATA, T. W. DIBBLEE, JR., and J. L. DRINKWATER

ABSTRACT

The Monterey Shale, here of Miocene age, is widely distributed east of the San Andreas fault around Cholame, Calif., at variable distances from the fault and from bodies of intrusive serpentinite. The basal part of the siliceous McLure Shale Member of the Monterey Shale contains disordered and intermediate cristobalite throughout the region except in restricted areas where it contains ordered cristobalite and (or) microquartz. The formation of microquartz required diagenetic temperatures at least 15°C above the general ambient of 65°C, and areas where the shale contains such microquartz and associated ordered cristobalite are termed "warm spots." The two largest warm spots are situated on or close to major magnetic anomalies previously described and interpreted in terms of large subsurface bodies of serpentinite. Warm water of the kind known to have altered and mineralized serpentinite elsewhere in the Coast Ranges probably warmed the overlying Monterey Shale sufficiently to bring about the transformation of cristobalite into microquartz. The presence of disordered cristobalite in shale adjacent to the San Andreas fault suggests that movements along the fault have not induced a sustained rise in temperature of even a few degrees in the shale.

INTRODUCTION

The diagenetic silica minerals of the middle Tertiary Monterey Shale of California are sensitive indicators of the temperature to which the shale has been subjected either through burial or hydrothermal alteration. The original metastable opal of diatom frustules in the shale eventually becomes transformed into stable quartz through intermediate cristobalite, and rates of transformation are strongly dependent on temperature. Exceptionally thick (>2.0 km) sections of the Monterey Shale well illustrate this temperature dependency by the presence of diagenetic quartz in the deepest and hottest zone, diagenetic cristobalite in an overlying zone of intermediate depth and temperature, and unaltered biogenic opal in the shallowest and coolest zone (Bramlette, 1946; Murata and Larson, 1975). The Monterey and other siliceous shales were source beds for much of California's petroleum, so information on the progressive diagenesis of the silica component of the shales may throw light on the transformation of associated organic matter into petroleum.

The proportions of diatom frustules, clay, and other constituents in the original sediment of the Monterey Shale varied greatly, from virtually pure diatomite through diatomaceous mud to mud. Diatomite alters diagenetically to bedded chert, a relatively pure silica rock, either cristobalitic or quartzose, which is dense and vitreous. The more common diatomaceous mudstone alters to porcelanite, a silica-cemented rock of either mineralogy which is less dense and vitreous than chert and is minutely porous so as to have a matte luster like that of unglazed porcelain (Bramlette, 1946). Mudstone alters to ordinary clay shale, which was not used in our studies because of its low content of diagenetic silica minerals. The above definitions of chert and porcelanite, based on texture rather than mineralogy, have been useful in describing the field relations of siliceous shale. Both chert and porcelanite are so fine grained that their mineralogy cannot be determined in the field but must be determined in the laboratory by means of X-ray diffraction or other laboratory procedures.

Whole-rock X-ray patterns of samples classified by us as chert in the field indicate that they are roughly more than 90 percent by weight diagenetic silica (either cristobalite or microquartz), and those classified as porcelanite about 70-90 percent. These limits are approximate because the diffractive power of diagenetic silica minerals is a function not only of their abundance but also of their grain size and degree of structural order, and because comparison standards for the X-ray estimates are perforce made by diluting "average" cristobalite ($d(101)\approx 4.08$A) or microquartz with clay shale.

Reconnaissance mineralogic study of the Monterey Shale by us during the past several years in many parts of California has shown that although opaline or quartzose samples predominate at some places, on a statewide basis cristobalitic chert and porcelanite are by far the most common. The same is true even among older siliceous formations, such as the Eocene and Oligocene Kreyenhagen Shale and the Upper Cretaceous and Paleocene Moreno Shale, in which a higher proportion of quartzose samples might be expected. Cristobalite, like the zeolites, was once considered a rare mineral in California that was confined mostly to volcanic rocks, but it is now known to occur as a major component of the widely distributed bodies of siliceous shale.

ACKNOWLEDGMENTS

We thank the ranchers of the study region for their courtesy in allowing us access to their lands. Helpful advice regarding the geology of serpentinite and mercury deposits was received from E. H. Bailey, R. G. Coleman, R. A. Loney, and D. E. White. R. W. Boyer and Marjorie G. Jones helped greatly with the laboratory work, and Elizabeth F. Murata assisted with the field work.

FACTORS THAT AFFECT TRANSFORMATION OF SILICA AND THEIR BEARING ON SAMPLE SELECTION

The overall rates of polymorphic transformation of silica are controlled primarily by temperature, as shown by the field relations described above and by the results of many laboratory investigations (Heydemann, 1964; Ernst and Calvert, 1969; Mizutani, 1970; Bettermann and Liebau, 1975; and Oehler, 1976, among others). Composition of the host sediment is also a factor. For example, the transformation tends to be accelerated in calcareous sediments (Lancelot, 1973; Garrison and others, 1975; and Keene, 1975). This effect is well illustrated by the faster conversion of cristobalite to quartz in the calcareous facies than in the clayey facies of deep-sea Cretaceous sediments from the North Pacific (Keene, 1975).

Similarly, the initial change of relatively pure diatomite into cristobalitic chert proceeds more rapidly than does the change of associated diatomaceous mudstone into cristobalitic porcelanite (Mulryan, 1936; Kastner and others, 1977). This early effect of clay and other impurities persists in the subsequent structural ordering of cristobalite, in which the d(101) spacing of chert tends to be about 0.01A larger than that of associated porcelanite. In using siliceous shale as a means of studying the diagenetic history of a sedimentary basin, these complications must be minimized by rejecting carbonate-rich material through field tests with acid and by selecting porcelanite of roughly the same content of a diagenetic silica mineral through the criteria of texture and hardness.

When first formed from opal, cristobalite has a disordered structure that gradually changes into the ordered structure of alpha-cristobalite (Floerke, 1955; Jones and Segnit, 1971). During the ordering process, the d(101) X-ray spacing of cristobalite contracts at a temperature-dependent rate from 4.11 to 4.04A (Murata and Nakata, 1974; Mitsui, 1975; Mizutani, 1977), as exemplified by porcelanite (fig. 1) from the Monterey Shale of the Temblor Range, Calif. The changing d(101) spacing provides a continuous diagenetic scale for siliceous shale over the temperature range of approximately 50°-80°C.

Lateral rather than vertical variation of d(101) spacing is of moment in a regional study of a bed of siliceous shale. Thus, vertical variations of the kind shown in figure 1 must be held to a minimum by collecting as much as possible from a single stratigraphic zone. A 100-m-thick bed of fairly uniform composition deposited over a large area would be ideal because such a bed is not thick enough for the d(101) spacing of its cristobalite to vary much (<0.01A) vertically. For purpose of further discussion, diagenetic cristobalite is subdivided into three structural categories and ranges of d(101) spacing,

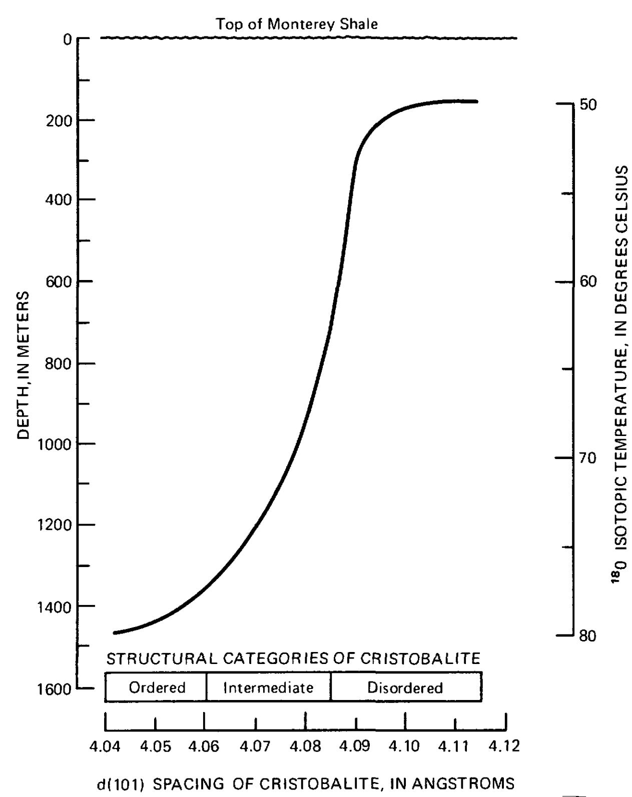

FIGURE 1.—Relation of d(101) spacing of cristobalitic porcelanite to depth of burial, to correlative temperature, and to threefold structural categories of cristobalite. Based on samples from Temblor Range, Calif. (Murata and others, 1977).

namely, disordered, 4.115-4.086A; intermediate, 4.085-4.061A; and ordered, 4.060-4.040A (fig. 1).

PRELIMINARY INDICATIONS OF TEMPERATURE ANOMALIES IN SILICEOUS SHALE CAUSED BY SERPENTINITE

The first indication that a large body of serpentinite might affect the diagenesis of an adjacent siliceous shale was found in a recent regional study by us of the Marca Shale Member of the Upper Cretaceous and Paleocene Moreno Shale. The Marca Shale Member (Payne, 1951) is a relatively thin (100-200 m), widely distributed Upper Cretaceous siliceous unit that crops out from Coalinga (comparison area, north part of fig. 2) to and beyond Vallecitos and to the north and west of the Ciervo Hills. Over a total distance of 120 km sampled by us, the unit is cristobalitic except for an interval 20 km long adjacent to the north margin of the New Idria serpentine piercement (Eckel and Myers, 1946), where it is quartzose. The higher temperature (>80°C) apparently sustained by the quartzose interval cannot be ascribed to the Marca Shale having been buried deeper there than elsewhere.

A second area where serpentinite may have affected the diagenesis of siliceous shale is a zone about 3 km wide and 35 km long extending from southeast of Smith Mountain to somewhat beyond Priest Valley (also in comparison area of fig. 2). The siliceous rock here is the Miocene Monterey Shale in an unusual setting dominated by Mesozoic Franciscan rocks and accompanying serpentinite. The Monterey Shale either lies directly on the Franciscan Formation and serpentinite or is separated from them by a few hundred meters of Cretaceous to middle Miocene sedimentary rocks (Pack and English, 1915; T. W. Dibblee, Jr., unpub. maps). Of the 35 samples of porcelanite collected over the area, 33 are quartzose and 2 are ordered cristobalitic, with a d(101) spacing of 4.06A. Here, also, the prevalence of quartzose shale cannot be explained in terms of excessive depth of burial under younger sediments.

These indications were sufficiently encouraging for us to undertake a closer study of the relations between the serpentinite and siliceous shale in an area around the village of Cholame and east of the San Andreas fault (bottom part of fig. 2) where the Monterey Shale and Franciscan rocks with accompanying serpentinite crop out in many places. The area is a southern extension of the above-mentioned regions already examined by us, and its geologic and geophysical aspects have been studied in detail by one of us (T. W. Dibblee, Jr.) and others.

GEOLOGY AND TECTONICS OF THE CHOLAME AREA

The complex geology of the Cholame area (pl. 1) has been studied by Bailey (1942), Stewart (1946), Marsh (1960), Dickinson (1966a, 1966b), Hanna, Burch, and Dibblee (1972), and Dibblee (1974), among others. Highly sheared Franciscan sedimentary and volcanic rocks of Mesozoic age and bodies of serpentinite are overlain by strongly folded Cretaceous and Tertiary sedimentary rocks and locally deformed Quaternary valley deposits.

The axis of the Diablo Range divides the area into two parts of contrasting sedimentology and tectonics. In the northeastern part, the Franciscan rocks and accompanying serpentinite are generally separated from Monterey Shale by a great thickness of intervening Mesozoic and Cenozoic rocks, so that, except in Avenal Canyon at the northwest end of McLure Valley syncline, there is little chance of any interaction between serpentinite and the Monterey Shale. In the southwestern part, the cover of later rocks is much thinner over the Franciscan, so that serpentinite and the Monterey Shale occur close together at many places. Folding and faulting of strata are more intense here than in the northeast area, probably because of proximity to the San Andreas fault (Hill and Dibblee, 1953; Dibblee, 1966; Dickinson, 1966b; Harding, 1976).

Serpentinite of the Cholame area seems to have been intruded cold (<500°C) into major fault zones (Bailey, 1942), and it crops out in the form of trains such as those that mark the Aido Spring thrust fault, 10 km east of Cholame. The large exposure of serpentinite in Table Mountain, 20 km north of Cholame, is highly sheared extrusive serpentinite (Dickinson, 1966a) that forms a carapace over feeder dikes and a major elongate intrusive body (Hanna and others, 1972).

Sampling of porcelanite in the Monterey Shale of the Cholame area was restricted to the basal part of the siliceous McLure Shale Member as mapped by Dibblee (1974, and unpub. maps). In the laboratory, each sample was first characterized by means of a whole-rock X-ray diffractogram, and those found deficient in diagenetic silica minerals were eliminated. The d(101) spacing of the cristobalitic samples was then determined by using the $(10\bar{1}1)$ peak of added quartz as internal standard (Murata and Larson, 1975).

DEGREES OF DIAGENESIS

GENERAL ASPECTS

Of the total of 121 samples collected from the Cholame area, none contains opaline remains of

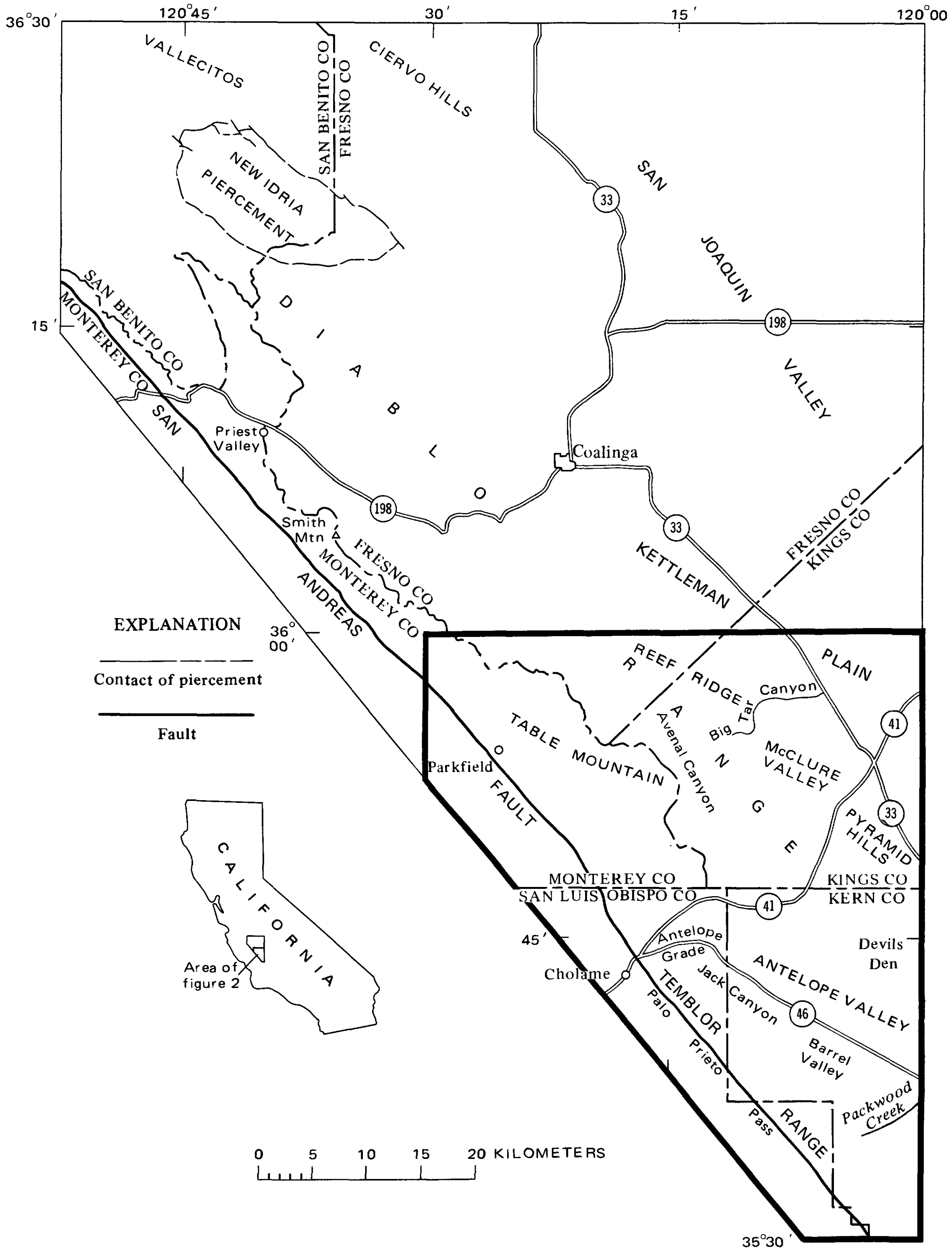

FIGURE 2.—Geographic features of area studied (outlined by heavy line) and comparison area to north.

diatoms, 107 are cristobalitic, and 14 are quartzose. The total absence of unaltered remains of diatoms suggests that the Monterey Shale here was generally exposed to a minimum temperature of about 50°C (approximate temperature derived from fig. 1). On the other hand, the occurrence of quartzose samples only in restricted serpentinite-rich sections of the area, to be discussed below, suggests that the maximum temperature was generally less than 80°C. In the further discussion of diagenesis we distinguish between regional diagenesis, seen in broad areas of disordered and intermediate cristobalite, and localized warm-spot diagenesis, seen in areas dominated by ordered cristobalite and associated microquartz. The crystallinity index of the quartzose samples (Murata and Norman, 1976) is uniformly low, ranging from 1.6 to 2.4 with a mean of 2.1.

REGIONAL DIAGENESIS

An overall index of regional diagenesis, useful for comparing different parts of the region and for comparing the Cholame region with other regions, can be stated in terms of the d(101) spacing of 94 samples collected outside of the warm spots; this spacing ranges between 4.064 and 4.105A. The average value is 4.083A, which falls high in the range for intermediate cristobalite and corresponds to a diagenetic temperature of 65°C (fig. 1).

Among samples of disordered and intermediate cristobalite that characterize regional diagenesis, the distribution of disordered cristobalite indicates places where the depth of burial of the Monterey Shale was the shallowest. Large areas of disordered cristobalite (pl. 2) are found in the syncline east of the village of Parkfield and in the area of Packwood Creek, 24 km northwest and 27 km southeast of Cholame, respectively, and in three small patches in between. The only known occurrence to the east of the main axis of the Diablo Range is a small area near Devils Den. This prevalence of disordered cristobalite of shallower burial in the southwestern part is reflected in the greater index of regional diagenesis (average d(101) spacing of samples with disordered and intermediate cristobalite) of 4.085A, corresponding to a temperature of 62°C there, compared to 4.078A and a temperature of 70°C for the northeastern part. The index for the southwestern part would be even greater and the temperature lower if some allowance could be made for samples in the immediate vicinity of the more extensive warm spots. The disordered cristobalite of the Parkfield syncline also indicates that warm spots are not likely to develop in siliceous shales underlain at shallow levels by "basement" Franciscan rocks that are poor in serpentine (cross section *A-A′*, pl. 4).

The d(101) indication that the general depth of burial was shallower in the southwestern part agrees with the known lesser thickness there of post-Monterey marine formations, as shown in cross section *A-A′* (pl. 4). The irreversibility of the diagenetic trend toward smaller d(101) spacing makes it very unlikely that the overburden atop the Monterey to the southwest was ever as thick as to the northeast. The lesser overburden in the southwestern part was probably the consequence of the more frequent and intense tectonic activity there throughout the Tertiary (English, 1919; Henny, 1927; and Dickinson, 1966b), which resulted in lesser net accumulation of sediment.

The Monterey Shale that bears disordered cristobalite in the southwestern part might also throw light on thermal characteristics of the San Andreas fault. Such shale occurs at various distances from the fault (pl. 2), 7-9 km away in the area of Packwood Creek, 5-7 km away at the southeast end of the Parkfield syncline, and virtually in contact with the fault toward the northwest end of the syncline. But no systematic spatial variation of the d(101) spacing with distance from the fault is evident in these occurrences. Thus, movements on the San Andreas fault apparently have not generated a sustained rise in temperature of even a few degrees in adjacent shale, a conclusion in harmony with the lack of well-defined heat-flow anomalies near large strike-slip faults of California (Henyey and Wasserburg, 1971).

WARM-SPOT DIAGENESIS

"Warm spots" are areas in which the shale contains mostly ordered cristobalite or microquartz indicative of exposure to a higher temperature than shale of adjacent areas. A major warm spot occurs in the northeastern part around Avenal Canyon (pl. 2) and is here called the Avenal Canyon warm spot.

Two others occur in the southwestern part, one north of the Antelope Grade on highway 46 and the other southwest of Jack Canyon and Barrel Valley. The latter elongate area is referred to as the Palo Prieto warm spot because of its relation to the Palo Prieto magnetic anomaly, previously described and named by Hanna, Burch, and Dibblee (1972).

The possibility that the Avenal Canyon warm spot was caused by tectonic deformation is suggested by the localization of the spot at the constricted northwest end of the McLure Valley syncline, where strata dip vertically in comparison to dips of 50°-75° in the more open parts. A vertical dip of strata is commonly thought to denote rather severe deformation, but whether there is a commensurate generation of heat and rise of temperature during such deformation is unknown. Elsewhere, such as the southwest side of Vallecitos (upper part of fig. 2), siliceous shale dips vertically or is even overturned (Pinkerton, 1967) but it contains disordered cristobalite with d(101) of 4.09A. Thus, there is no consistent relation between the silica-indicated stage of diagenesis and the attitude of the host bed.

There is also no indication that the McLure Shale Member was once buried more deeply in the Avenal Canyon warm spot than in immediately adjacent areas. Similar negative conclusions hold for the Palo Prieto warm spot, so the origin of such spots cannot be explained in terms of any extraordinary mechanical-thermal effects of deformation or of excessive depth of burial of the shale.

Both the Avenal Canyon and the Palo Prieto warm spots are situated within areas of major magnetic anomalies (pl. 1 and 3), which Hanna, Burch, and Dibblee (1972) have ascribed to large subsurface bodies of serpentinite. The warm spot north of Antelope grade on highway 46, while just outside the Palo Prieto magnetic anomaly, is probably an offshoot of the Palo Prieto warm spot.

The aeromagnetic data (pl. 1) were obtained through a flight pattern of seven traverses 6 km apart parallel to the San Andreas fault; the middle flight line followed the surface trace of the fault. The ground magnetic survey (pl. 3) covered the southern part of the area in greater detail and located the Palo Prieto anomaly more accurately than the aeromagnetic survey. The position of the Palo Prieto warm spot is seen to coincide with the zone of maximum intensity within the serpentinite-generated magnetic anomaly (pl. 3). Thus, in agreement with previous observations at the New Idria piercement and the Smith Mountain-Priest Valley region, siliceous shale of the Cholame area shows abnormally advanced diagenesis wherever it overlies large bodies of serpentinite.

The way warm spots are situated with respect to subsurface bodies of serpentinite is well shown in the two cross sections *A-A′* and *B-B′* (pl. 4. after Hanna and others, 1972). Cross section *B-B′* happens to pass through a gap in the outcrop of the Monterey Shale within the Palo Prieto warm spot (pl. 2), so it is necessary to consider all samples 2.5 km on either side of *B-B′* in order to show how the degree of silica diagenesis varies along the entire section. The maximum and minimum degrees of diagenesis along the section are shown in plate 4 under the heading, "Silica mineralogy and d(101) spacing of cristobalite." Likewise for section *A-A′*, the indicated maximum and minimum degrees of diagenesis are based on samples from a zone 2.5 km on either side of the section.

A body of intrusive serpentinite warming nearby rocks is roughly comparable to an igneous intrusion causing contact metamorphism, although the rise in temperature of the affected rock would be far less. The temperature of the average cristobalitic shale of the Cholame area need have been raised only to about 80°C from an ambient temperature of about 65°C and held at 80°C for 250,000 years in order for cristobalite to be transformed into quartz (Ernst and Calvert, 1969). At 100°C, 36,000 years would have sufficed for the transformation.

INTRUSIVE SERPENTINITE AS A SOURCE OF HEAT

The following discussion of the ways in which intrusive serpentinite could warm adjacent rocks is based mostly on the highly sheared serpentinite of Table Mountain. This rock is believed to have been serpentinized at depth and, before its intrusion and extrusion during the Pliocene and Pleistocene orogeny, was injected and stored within the Franciscan Formation (Dickinson, 1966a). The outcrop area of the serpentinite, shown in plates 1 and 3, represents about half of the relatively small volume (2.0 km^3) of serpentinite that reached the surface and formed a carapace over a large tabular intrusive body of serpentinite with an average width of 4.0 km and a total volume of roughly 600 km^3 (Hanna and others, 1972). We shall use the spatial relations between the intrusion and the Monterey Shale of the Avenal Canyon warm spot as depicted in section *A-A′* (pl. 4) to compute the thermal effects of the intrusion. The computed results will tend to err on the low side, because the section happens to cut the intrusion where it is abnormally thin (0.6 km).

The initial temperature of the intrusion is roughly determined from the following considerations. If the serpentinite rose quickly from a place of storage at depths of 10-14 km (the latter being the maximum depth considered in pl. 4), the initial temperature could have been around 300°-450°C, based on a geothermal gradient of 30°C/km (Moses, 1962). Existing data on serpentinization of ultramafic rocks further suggest that most serpentinite of orogenic zones probably formed in the temperature range of 100°-300°C (Coleman, 1971; Coleman and Keith, 1971). Thus, 300°C seems to be a reasonable initial temperature for the Table Mountain intrusion.

Lovering (1955) and Jaeger (1959) have computed temperature changes that are induced in a country rock through conduction of heat from a quickly intruded igneous dike. Their equations were adapted to the serpentinite intrusion by eliminating latent heat of fusion and by assuming that the thermal conductivity and diffusivity of serpentinite were equal to or greater than those of the country rock (Jaeger, 1959, table 1, fig. 1). If the initial temperature of the intrusion were 300°C, the greatest distance at which the temperature of the country rock would be raised 15°C above the ambient of 65°C would be about 1.2 km from the edge of the intrusion. This result is a crude approximation, but it suggests only a marginal chance for the Monterey Shale of Avenal Canyon, which is 1 km from the dike, to become hot enough to form quartz solely by heat conduction through intervening rock. On the other hand, the larger size of the Palo Prieto intrusion (pl. 4, section *B-B'*) makes it more likely that the temperature of the overlying Monterey Shale would be raised sufficiently by conducted heat alone.

Another way that the Table Mountain serpentinite could have heated overlying rocks is by the intrusion serving as a conduit for hot water rising from depth. The former existence of a hot water system at Table Mountain is indicated by the extensive post-emplacement alteration of the serpentinite to silica-carbonate (magnesite) rock, which in turn became the host rock for substantial deposits of mercury (Bailey, 1942; Bailey and others, 1964). The production of silica-carbonate rock involved solutions with temperature in the range of 15°C to 100°C (Barnes and others, 1973); only solutions hotter than 80°C would be pertinent to the origin of a warm spot.

Avenal Canyon mine, a prospect for mercury, is situated within the warm spot, but no commercial production is recorded for the mine. Estimates of temperature of formation of mercury deposits fall mostly in the range of 50°C to 280°C (Bailey and Everhart, 1964; White, 1967; Dickson and Tunell, 1968). Fluid inclusions in quartz associated with mercury deposits of the McDermitt Caldera, Nevada-Oregon, yield depositional temperatures of 195°-205°C (Rytuba, 1976). Offshoots from the intrusion (section *A-A'*, pl. 4) could have channeled hot rising waters toward Avenal Canyon to create the warm spot and to accelerate the cristobalite-microquartz transformation there. Hanna, Burch, and Dibblee (1972) found that the geophysical data required the intrusion to dip to the northeast, and this dip makes the intrusion pass under Avenal Canyon, thereby greatly increasing the chance of any fluid emanating from the intrusion to warm the overlying Monterey Shale.

With warm waters flowing mostly through a limited number of channels for a limited time, the warming of a siliceous shale could be rather uneven compared to the more uniform warming by rock-conducted heat and could result in fluctuation in silica mineralogy to the extent seen within the major warm spots. The warm spot of Palo Prieto probably originated much in the same way as that of Avenal Canyon. These results suggest that should interest ever develop in locating hidden bodies of serpentinite (perhaps in a search for mercury deposits) in areas containing siliceous shale, a study of the silica mineralogy of the shale would be a useful supplement to magnetic surveys.

Finally, brief comments will be made on three minor warm spots (marked by ordered cristobalite or microquartz), two along Reef Ridge and one at the southeast end of the Parkfield syncline (pls. 2 and 4). The single quartzose sample from the extreme northwestern part of Reef Ridge is the southernmost representative of the previously mentioned quartzose shale that is predominant in the Smith Mountain-Priest Valley area. The lone sample of ordered cristobalite at Big Tar Canyon may have been affected by a unique hydrothermal event that cemented the underlying sandstone of the Temblor Formation with analcime. The two samples from the Parkfield syncline bearing ordered cristobalite are anomalous. Their situation at the end of syncline and along a major fault may have subjected them to mild localized heating of some kind.

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