## Reports

## **Two-Billion-Year Granulites in the Late Precambrian Metamorphic Basement Along the Southern Peruvian Coast**

Abstract. Uranium-lead data indicate that the high-pressure granulitic and charnockitic nuclei within the medium-grade metamorphic complex of the Peruvian coastal area must be related to an orogenic event  $2 \times 10^9$  years ago. As in western Africa and Brazil, this old granulitic basement is reworked by Late Precambrian orogeny. Its presence along the Peru-Chile Trench must be taken into account in interpreting the anomalously high strontium isotopic ratios of recent calc-alkaline volcanism.

The Peruvian Andes between the Brazilian shield and the Peru-Chile Trench are a complex mountain system made up largely of rocks deformed by Precambrian, Hercynian, and Andean orogenies (1). Precambrian rocks exposed in the eastern Andean cordillera and along the southern Peruvian coast (Fig. 1) (2) form part of a single Late Precambrian orogenic belt (3-5). They are characterized by the same overall lithology and polyphase deformation and by two metamorphic events (6), the first of intermediate pressure and the second of low pressure. From place to place, and especially along the southern coast, these medium- to high-grade mobilized metamorphic rocks are associated with older granulites and charnockites.

The medium- to high-grade metamorphic Precambrian terranes of the southern Peruvian coast are composed of a thick lower metasedimentary sequence, interbedded with basic gneisses, and an upper series of prasinitic schists. These rocks were strongly deformed during two periods of Precambrian isoclinal folding.

The oldest and most important deformation is contemporaneous with the first prograde metamorphism. The second is associated with the general retrograde metamorphism, the regional cleavage, and the fold lineation transverse to the coast. Two later compressive events that produced chevron folds and kink bands end the Late Precambrian orogeny. The first prograde metamorphism seems to increase in grade toward the south. It is generally characterized by biotitestaurolite, garnet-kyanite-sillimanitepotassium feldspar relict associations of a medium-pressure type with cordierite in catazonal paragenesis. By comparison with similar Precambrian rocks of the eastern cordillera (6), the metamorphic gradient is typically Barrovian. The second metamorphism, of a low-pressure type (chlorite-muscovite-epidote-cordierite), corresponds to a general epizonal retrograde metamorphism.

Important nuclei of various granulitefacies rocks are exposed along the southern part of the Peruvian coast (Camana to Mollendo) within the younger Precambrian rock sequence described above. Several rock types have been rec-



Fig. 1. Map showing the general location of Precambrian rocks in Peru; arrows indicate the source locations of samples from the southern coast that were studied.

ognized: (i) a khondalite-kinzigitic sequence (7, 8) (quartzites, khondalites, kinzigites, and  $Al_2SiO_5$ -free granulites), (ii) various layered stromatic charnockitic paragneisses in which hypersthene and sillimanite coexist, (iii) enderbitic gneiss (9), (iv) two-pyroxene granulites and hornblende granulites, and (v) dolomitic marbles.

The mineral assemblages of these rocks show that the older granulitefacies metamorphism belongs to the intermediate high-pressure type of Green and Ringwood (10). Incipient retrograde postkinematic corona textures (associated with the kyanite-sillimanite transition) suggest (11) a slight uplift after the granulite metamorphism but before the Late Precambrian orogeny. This older catazonal complex was strongly affected by the epizonal retrograde metamorphism referred to above.

One or two size fractions of zircons weighing from 0.3 to 5 mg each have been separated from specimens of the granulite-facies rocks. We analyzed the samples from 0.5 to 2 mg by digestion in a 200- $\mu$ l Teflon microbomb (12) with HF, followed by the isolation of uranium and lead by anion exchange in columns of AGIX8 resin (13). For the smaller (0.3 mg) samples, we used a procedure similar to the one reported (14) for grain-bygrain zircon analysis; silica gel was added for the lead analyses, and a portion of the spiked sample was deposited directly on a triple filament source for the uranium analyses.

The samples that we studied have quite low uranium and lead contents (Table 1). The results of the analytical work are presented graphically (Figs. 2 and 3) in concordia diagrams (<sup>206</sup>Pb/<sup>238</sup>U versus <sup>207</sup>Pb/<sup>235</sup>U). The zircon data points define a colinear array, and the upper and lower intercepts with the concordia curve give, respectively, ages  $T_1$  of 1910 ± 36 × 10<sup>6</sup> years and  $T_2$  of 720 ± 29 × 10<sup>6</sup> years. Decay constants used in the calculation were  $\lambda_{238_U} = 0.15525 \times 10^{-9}$  year<sup>-1</sup> and  $\lambda_{235_U} = 0.98485 \times 10^{-9}$  year<sup>-1</sup> (15).

If a simple episodic lead loss model is used (16), the data agree with geological field studies and petrological observation if we relate the intermediate high-pressure granulite metamorphism to  $T_1$  (an orogenic event  $2 \times 10^9$  years ago). The Late Precambrian orogeny (the so-called Pan-African or Brazilide event) would be responsible for episodic lead loss. Nevertheless, this interpretation is too simple, especially since the lower intercept appears to indicate an age slightly too old. Other simple models of continuous lead loss (17, 18) have been used to compute lead loss starting at  $T'_1$  (1.9 ×10<sup>9</sup> years  $\leq T'_1 \leq 2 \times 10^9$  years) and stopping at  $T'_2$  (0.6 × 10<sup>9</sup> years  $\leq T'_2 \leq 0.66 \times 10^9$  years). Good fits (Fig. 2) of the calculated discordia curves with experimental points are obtained in these cases, but the best fits are obtained if multistage models are used (*19*) (Fig. 3) with the sequence: (i) continuous lead loss from  $T'_1$  to  $T'_2$ , (ii) episodic lead loss at  $T'_2$ , and (iii) a closed system from  $T'_2$  to the present time.

We thus prefer the latter interpretation, and we assign an age of about  $1.95 \times 10^9$  years to the granulite-facies metamorphism; from this time to about  $0.6 \times 10^9$  years the granulite-facies rocks remained in the deep zone of the continental crust and underwent a strong continuous lead loss. Uplift and retrometamorphism occurred during Late Precambrian orogenesis, producing a slight episodic lead loss.

These results have three important implications:

1) An orogenic event  $1.9 \times 10^9$  to  $2.1 \times 10^9$  years ago that produced gran-

ulite charnockite rocks, reworked as nuclei in the Late Precambrian without evidence of an intermediate event  $1 \times 10^9$ years ago, seems to be a widespread phenomenon in South America, as well as in west and central Africa. In western Ahaggar (Algeria), for example, the granulite metamorphism of the In'Ouzzal formation, which is a basement unit occurring in the Pan-African orogenic belt, limited by large shear zones, has been dated at  $2.05 \times 10^9$ years on the basis of old uranium decay constants (14, 20). Furthermore, data from zircons studied grain by grain and whole-rock rubidium-strontium from studies (21) have shown that these metasedimentary sequences derive from rocks that are  $3.1 \pm 0.1 \times 10^9$  years old. A similar sequence is known in Brazil, where, for example, the parametamorphic granulite of Paraíba do Sul produced  $2 \times 10^9$  years ago (22) was reworked during the Late Precambrian orogeny (Serra dos Orgaos gneisses) (23). These granulite rocks from Brazil also seem to have been derived from terranes  $3.1 \times 10^9$  years old (Mantiqueira and Barbacena gneisses) (23).

2) The uranium-lead results presented here also indicate a Late Precambrian event along the southern Peruvian coast; this conclusion is supported by geological relations in the area of Rio Majes (north of Mollendo), where weakly deformed Devonian sediments unconformably overlie the strongly folded Precambrian metamorphic complex (24). Identical field relationships have been recognized at other places in the eastern cordillera (3, 25).

The Late Precambrian thermal event deduced from lead loss models (Figs. 2 and 3) is also in agreement with the potassium-argon data of  $642 \pm 16 \times 10^6$ and  $679 \pm 12 \times 10^6$  years (5) obtained for the Arequipa granitoid and basic gneisses. Furthermore, a potassium-argon age of  $647 \times 10^6$  years has been reported (26) from orthogneiss xenoliths included in Tertiary volcanites from northwestern Bolivia; these orthogneisses could possibly belong to a southeastern extension of the Arequipa

Table 1. Uranium and lead contents of the granulitic and charnockitic nuclei. Common lead values used for blank correction:  ${}^{206}Pb/{}^{204}Pb = 18.5$ ;  ${}^{207}Pb/{}^{204}Pb = 38.0$ . Mean calculated errors: 0.9 percent for ( ${}^{206}Pb/{}^{238}U$ ); 1.1 percent for ( ${}^{207}Pb/{}^{235}U$ ). Samples: PB 159, enderbite; PB 167, charnockite; PB 174, charnockite paragneiss; PB 173, khondalite; ppm, parts per million.

Sample	Sample weight (g)	U (ppm)	Pb (ppm)	<sup>206</sup> Pb/ <sup>204</sup> Pb (measured)	<sup>207</sup> Pb/ <sup>206</sup> Pb (corrected)	<sup>206</sup> Pb/ <sup>238</sup> U (corrected)	<sup>207</sup> Pb/ <sup>235</sup> U (corrected)
PB 159 (200 mesh)	0.00207	449	140	3436	0.11213	0.2939	4.5413
PB 167 (200 mesh)	0.00106	543	163	1478	0.11233	0.2925	4.5280
PB 174 (200 mesh)	0.00213	232	159	4365	0.10466	0.2375	3.4187
PB 174 (200 mesh)	0.00308	230	58	6768	0.10464	0.2386	3.4404
PB 174 (100 mesh)	0.00100	257	64	1600	0.10372	0.2376	3,3959
PB 173 (300 mesh)	0.00033	273	53	1408	0.09401	0.1884	2.4463



Fig. 2 (left). Concordia diagrams,  $^{209}\text{Pb}/^{238}\text{U}$  versus  $^{207}\text{Pb}/^{235}\text{U}$ . The line labeled 2 represents the best straight line obtained by a two-error regression treatment. The diffusion curve (labeled 1) is obtained by assuming a continuous lead loss (17) from  $1.95 \times 10^9$  to  $0.6 \times 10^9$  years and a closed system from  $0.6 \times 10^9$  years until now. Fig. 3 (right). Concordia diagram,  $^{206}\text{Pb}/^{238}\text{U}$  versus  $^{207}\text{Pb}/^{235}\text{U}$ . A multistage model is assumed with continuous lead loss between  $T'_1 = 1.95 \times 10^9$  years and  $T'_2 = 0.6 \times 10^9$  years, episodic lead loss at  $T'_2$ , and a closed system between  $T'_2$  and the present time. Variations in parameter A (19) permit determination of the relative importance of episodic and continuous lead losses. For  $0.001 \le A \le 0.01$  (models 3 and 4) the episodic lead loss is negligible as compared to the continuous lead loss; the inverse is obtained for A = 1 (model 6). For model 5, which shows a good fit to the data, A = 0.1.

complex. Farther to the south, rubidiumstrontium whole-rock ages between  $600~\pm~50~\times~10^{6}$  $500 \pm 35 \times 10^{6}$ and years have been reported (27) from the Pampean ranges of northwestern Argentina. They could also be related to the Late Precambrian orogeny, if we consider that the numerous Hercynian granitoid intrusions in this area have produced thermal effects that may have opened the rubidium-strontium system of the Late Precambrian rocks with quite high rubidium-strontium ratios (28).

3) The presence of the granulitecharnockite complex  $2 \times 10^9$  years old along the Peru-Chile Trench must be taken into account in genetic models of Andean volcanism. James et al. (29) and Hamet et al. (30) have suggested crustal contamination as a possible explanation for the variation of <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios (0.7055 to 0.7080) in recent calc-alkaline lavas (Arequipa and Barrosso units) erupted through the thick Peruvian continental crust; these data contrast with lower isotopic ratios (0.7030 to 0.7042) generally found in similar rocks associated with subduction zones, where the crust is intermediate or oceanic. New strontium isotopic measurements have been carried out on rocks of the same units (31). Evaluation in terms of "mixing models" (31, 32) of all these strontium data support the assumption that the observed high strontium isotopic ratios are due to a crustal contamination.

Note added in proof: While this report was in press, a paper by Cobbing et al. about similar Rb/Sr studies was published (33).

B. DALMAYRAC Laboratoire de Géologie Structurale, Office de la Recherche Scientifique et Technique Outre-Mer, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France

J. R. LANCELOT Service Commun de Géochronologie et de Géochimie Isotopique, Université des Sciences et Techniques du Languedoc

A. LEYRELOUP Laboratoire de Pétrologie, Université des Sciences et Techniques du Languedoc

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## **Cancer Mortality in U.S. Counties with Petroleum Industries**

Abstract. A survey of cancer mortality from 1950 to 1969 was conducted in U.S. counties where the petroleum industry is most heavily concentrated. Male residents of these counties experienced significantly higher rates for cancers of the lung, the nasal cavity and sinuses, and the skin (including malignant melanoma) compared to male residents of counties with similar demographic characteristics. Further study is needed to determine whether these patterns result from exposure to chemical carcinogens, including polycyclic hydrocarbons, involved in the manufacturing of petroleum.

Polycyclic aromatic hydrocarbons (PAH) are found in crude petroleum, in the high boiling residues of catalytically cracked oils, in other pyrolysis products, in soots, and in air surrounding refining operations (1). Although exposure to PAH in several occupational groups has induced cutaneous and pulmonary cancers in man (1, 2), there has been no clear indication that petroleum refinery workers are exposed to excess risk (3). However, indirect evidence of a hazard was suggested recently by a national survey of lung cancer mortality indicating that such mortality was higher among males in U.S. counties with petroleum manufacturing industries, and by a Los Angeles study correlating lung cancer rates in census tracts to airborne levels of PAH emitted, in part, from petroleum refineries (4). To evaluate this issue further, we compared the mortality rates from various cancers during 1950 to 1969

in U.S. counties involved in petroleum manufacture with the rates in a group of counties with similar demographic characteristics but no involvement in the industry.

A total of 604 U.S. counties had plants engaged in petroleum manufacture (standard industrial classification code 29) according to the 1963 Census of Manufactures, although there were less than 20 employees in over one-third of these counties (5). Selected for study were 39 petroleum-industry counties (PIC) where at least 100 persons were employed and where the estimated number of workers divided by the county population exceeded 0.01. The fraction employed reached 0.07 in one PIC but was usually under 0.02. It was 0.017 for the 39 PIC combined, involving about 50,000 petroleum workers. The number employed by sex was not available per county, but national statistics show a predominance of