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Strontium, Carbon and Oxygen Isotope Trends in the Pucará Basin, Peru: Brine Evolution and Formation of Mississippi Valley-Type Deposits

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Abstract: $^{87}Sr/^{86}Sr$ ratios increase gradually from early sedimentary to late diagenetic carbonate generations in the Pucará basin, central Peru. In parallel, O and C isotopes become lighter with the paragenetic sequence. The combined Sr-O-C isotopic data reveal that (1) early replacement dolomite precipitated from brines dominated by Upper Triassic and Lower Jurassic seawater; (2) late-stage sparry dolomite and coarse-crystalline calcite were deposited by ^{87}Sr-enriched, and ^{13}C- and ^{18}O-depleted brines most probably derived from detrital rocks at the base of the basin ; and (3) MVT deposits were formed by warm radiogenic brines, of similar origin, migrating over a considerable vertical distance from deep to shallow levels in the Pucará Group during the late diagenetic evolution of the basin.

Sr isotope geochemistry, along with O and C isotopes, is particularly useful in constraining the origin and flow paths of brines and mineralizing fluids in sedimentary basins, as well as to pinpoint the relative timing of diagenetic events in such basins, including ore-formation (Gorzawski et al. 1989; Kaufmann et al. 1990, 1991; Fontboté and Gorzawski 1990; Mountjoy et al. 1992). The Sr of secondary carbonates, associated with major sulfide mineralization in MVT deposits, is generally more radiogenic than in the host rocks. $^{87}Sr/^{86}Sr$ ratios tend to increase with the crystallization sequence of the secondary carbonates (Kessen et al 1981; Medford et al. 1983; Kesler et al. 1988; Gorzawski et al. 1989; Fontboté and Gorzawski 1990). The radiogenic Sr composition is generally interpreted as resulting from a mix between nonradiogenic Sr derived from the host rocks and radiogenic Sr leached out of rubidium-bearing minerals by the brine before it reached the site of metal deposition. Some studies have also shown a more or less pronounced progressive depletion of the isotopic composition of O and C with the paragenetic sequence of carbonates in MVT deposits (Ravenhurst et al. 1989; Fontboté and Gorzawski 1990; Ghazban et al. 1990).

Thus, local isotopic investigations on MVT deposits may allow us to unravel the mechanisms and the relative timing of ore-formation. However, since the genesis of MVT deposits is linked to the diagenetic evolution of the host sedimentary basin, such investigations need also to be carried out on a basin-wide basis to integrate the formation of these deposits within the regional geologic setting, notably to provide insights into the regional pathways of the mineralizing brines (Kesler et al. 1988; Ravenhurst et al. 1989). This contribution addresses the question of the relationship between the fluids that formed MVT deposits, and the migration and evolution of brines in a sedimentary basin. The purpose of this investigation is to determine whether or not there are local and regional geochemical patterns that may help resolving the genesis of MVT deposits within a broader geologic setting. The present study was undertaken in the Pucará basin, central Peru, a carbonate platform hosting several MVT deposits. Carbonates from ore-bearing (Shalipayco and San Vicente) and barren areas (Tingocancha, Malpaso and Tarma), and from different positions in the stratigraphic column have been analyzed for their Sr, C and O isotopic composition. The carbonates represent different subsequent evolution stages of the Pucará basin, spanning early sedimentary to late diagenetic events. They can be subdivided in two groups: (1) original and moderately diagenetically modified sedimentary rocks, including limestones, replacement dolomites and evaporites, and (2) late diagenetic carbonates, including white sparry dolomite and coarse-crystalline calcite.

GEOLOGICAL SETTING

The Pucará basin is an extensive Triassic-Jurassic carbonate platform located on the western margin of the Brazilian Shield in northern and central Peru. The Pucará Group was deposited at the beginning of the Andean cycle during marine transgression over clastic, sedimentary and volcaniclastic rocks belonging to the Late Permian to Early Triassic Mitu Group. The Pucará Group is subdivided from base to top into (Fig.1): (1) the Norian to Rhaetian Chambará Formation, (2) the Hettangian to Sinemurian Aramachay Formation, and (3) the Pliensbachian to Toarcian Condorsinga Formation. Shallow water deposits, including peritidal facies with evaporite development and abundant oolithical barriers, predominate across the entire basin, except in the Aramachay Formation which is characterized by deeper anoxic facies.

The geologic evolution of the Pucará basin resembles that of carbonate platforms in pericratonic areas. This basin is not or only marginally related to magmatic arc-back arc tectonics. Only the upper Aramachay Formation and the Condorsinga Formation appear to be coeval with a western subduction-related volcanic arc (Fontboté 1990). The thickness of the Pucará basin increases from west to east with distance to the Paleo-Pacific Ocean. A tectonic style of tilted blocks controlled by synsedimentary marginal faults is most certainly responsible for this morphology.

Zn-Pb MVT deposits occur mainly in the eastern part of the Pucará basin, at the base and within the Pucará Group, whereas Zn-Pb-(Cu-Ag) volcanic-associated deposits predominate in the western part of the basin at the contact between the Mitu and Pucará Groups (Fontboté 1990). The San Vicente mine is the largest MVT deposit. It is presently one of the major Zn producers of Peru with an accumulated production of about 14 million metric tons, reserves exceeding 4 million tons, and Zn and Pb grades of 11% and 0.8%, respectively. Geological and genetic aspects of this deposit are discussed by Fontboté and Gorzawski (1990).

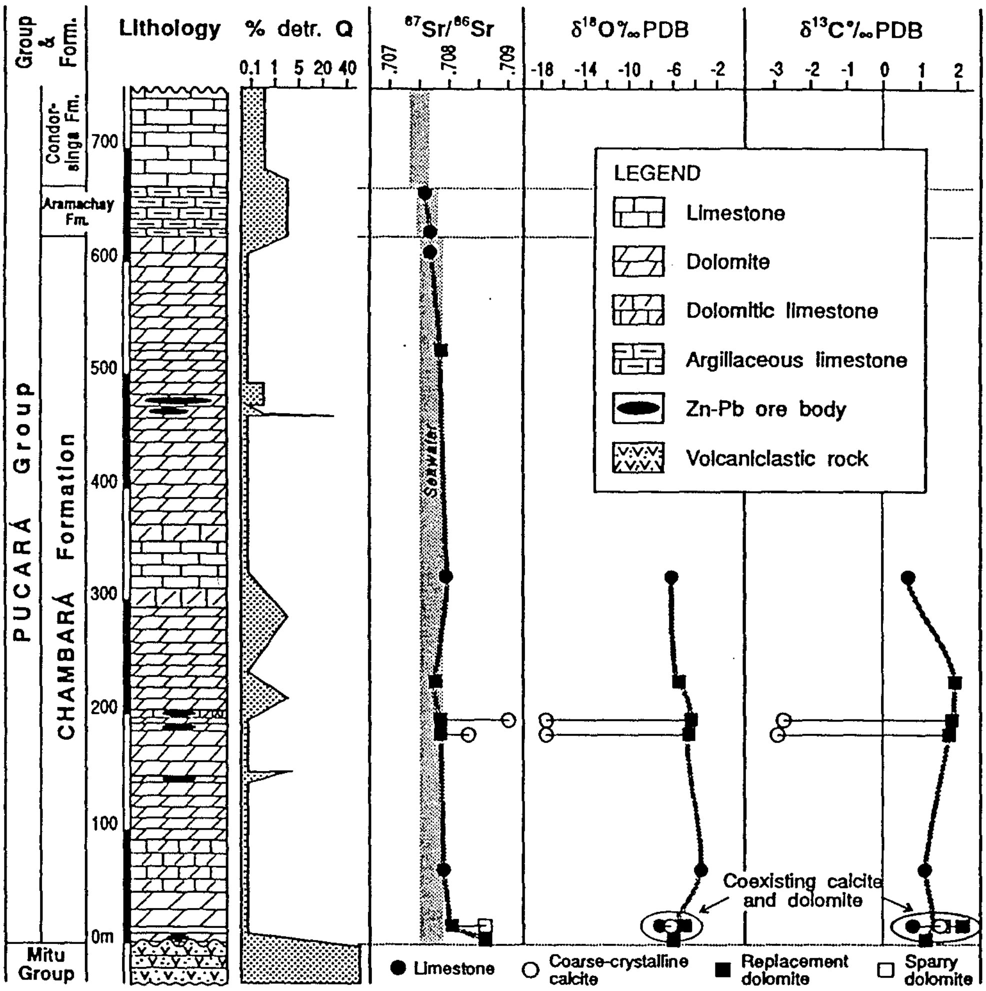

Figure 1. Profile of the Pucará sequence at Shalipayco with Sr, O and C isotopic trends.

LIMESTONES, REPLACEMENT DOLOMITES AND EVAPORITES

With the exception of carbonates from the base of the Chambará Formation and in the San Vicente mine area, gypsum, limestone and replacement dolomite samples yield ^{87}Sr/^{86}Sr ratios that fall within or close to the seawater ^{87}Sr/^{86}Sr values published by Koepnick et al. (1990) for the Lower Jurassic and the Upper Triassic (Figs.1 and 2). The δ^{13}C and δ^{18}O values of limestone and replacement dolomite from the Aramachay and Chambará Formations fall within the ranges -5‰ to 4‰ and -8‰ to 0‰ (PDB), respectively (Figs. 1 and 2), characteristic of Jurassic and Triassic sedimentary carbonate rocks (Veizer and Hoefs 1976). The combined Sr, O and C isotopic values suggest that the replacement dolomite was probably precipitated penecontemporaneously, at or below seafloor, from brines dominated by Upper Triassic and Lower Jurassic seawater.

The ^{87}Sr/^{86}Sr ratios gradually increase towards the bottom of the Chambará Formation, with the highest ratios at the immediate contact with the underlying detrital rocks of the Mitu Group (Fig.1). This trend indicates that ^{87}Sr-enriched fluids have migrated upwards into the Pucará Group, and that the most likely sources of radiogenic strontium are the detrital, volcaniclastic and volcanic rocks of the underlying Mitu Group, as well as red sandstones occurring at the base of the eastern Pucará Group.

The δ^{13}C and δ^{18}O values of limestones and replacement dolomites from the base of the Pucará Group do not differ from those of the carbonates from the rest of the sequence (Figs. 1 and 2), with the exception of one sample from the immediate contact between the Mitu and the Pucará Groups. Thus, while the Sr isotopic compositions of the carbonate rocks at the base of the Pucará sequence were altered by the incoming basinal brines, it appears that the latter essentially did not affect the C and O isotopic compositions. Recrystallized and secondary carbonates in general tend to inherit the C isotopic composition of the precursor carbonates, because very high water-rock ratios are required to alter the primary C isotopic composition of carbonates during diagenesis. In contrast, δ^{18}O values can be reset at relatively low water-rock ratios (Banner et al. 1988; Banner and Hanson 1990). A likely explanation for the unmodified O isotopic compositions at the base of the Pucará basin is that late high-temperature and ^{18}O-enriched brines can precipitate carbonates with a similar range of δ^{18}O values compared to earlier low-temperature, ^{18}O-depleted fluids.

Limestone from the younger Condorsinga Formation yields δ^{18}O values between -16.6‰ and -6.4‰ (PDB) that are lighter than normal Jurassic marine carbonates (Fig.2). The O isotope values most probably reflect meteoric water input either during diagenesis or during deposition of the Condorsinga carbonate sequence. The latter scenario is consistent with the predominance of very shallow water facies within the Condorsinga Formation.

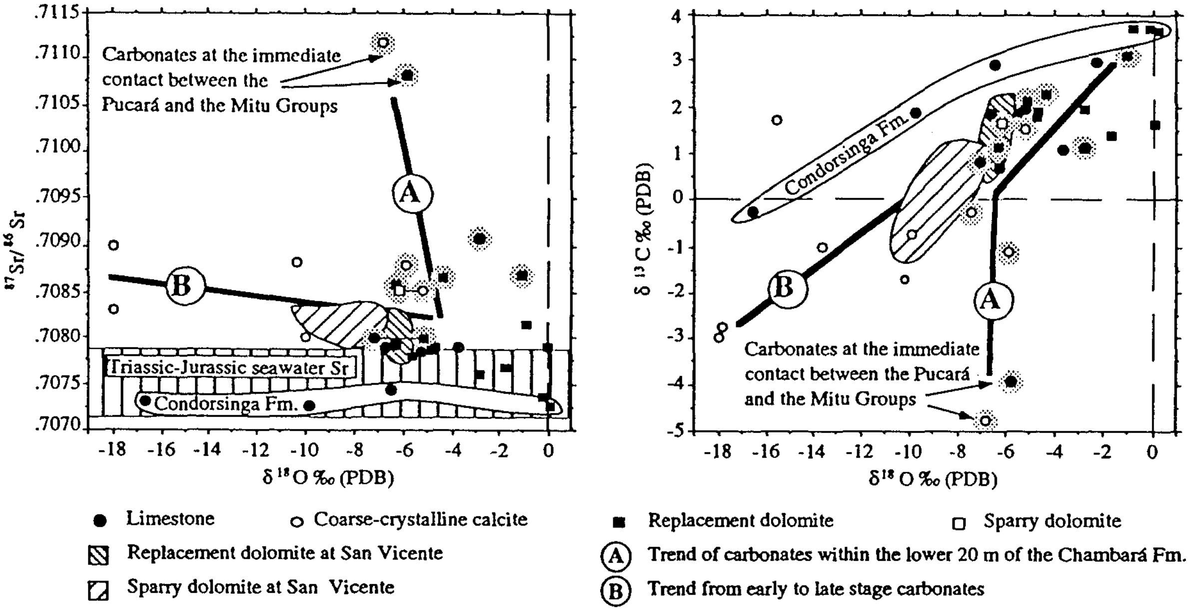

Figure 2. Covariance between Sr, O and C isotopic compositions of successive carbonate generations in the Pucará Group at Tingocancha, Malpaso, Tarma, Shalipayco and San Vicente.

LATE STAGE SPARRY DOLOMITE AND COARSE-CRYSTALLINE CALCITE

Late stage sparry dolomite and coarse-crystalline calcite yield systematically higher $^{87}Sr/^{86}Sr$ ratios and lighter $\delta^{13}C$ and $\delta^{18}O$ values than the immediate limestone or replacement dolomite (Figs.1 and 2). Sr of these late stage carbonates is more radiogenic than Sr of carbonates precipitated from Jurassic and Triassic seawater (Figs. 1 and 2).

As stated above, the radiogenic Sr is likely derived from the detrital rocks at the base of, and underlying the Pucará Group. The change towards lighter $\delta^{18}O$ values with the carbonate paragenetic sequence most probably reflects a gradual change in the isotopic composition of the precipitating brines accompanied by a concomitant temperature increase. Combined data from S isotope geothermometry (Fontboté and Gorzawski 1990) and preliminary fluid inclusion microthermometry (Moritz et al. 1992) at the San Vicente deposit are also in agreement with sparry dolomite being precipitated from a warm and saline brine during burial diagenesis.

The progressive lighter C isotopic composition with younger diagenetic phases reflects a change in the isotopic composition of the C reservoir and derivation of some C from organic matter. The local intimate relationship between some late stage carbonates, bitumen, sulfides and evaporite pseudomorphs, together with depleted $\delta^{13}C$ values suggests that thermochemical sulfate reduction may have contributed some of the C incorporated in coarse-crystalline calcite and sparry dolomite. This conclusion is supported by heavy and relatively homogeneous S isotopic compositions of sphalerite and galena at the San Vicente mine which indicate *in situ* H_2S production by abiogenic sulfate reduction (Fontboté and Gorzawski 1990). Alternatively, it cannot be excluded that the light $\delta^{13}C$ and $\delta^{18}O$ values and the radiogenic Sr isotopic composition of some late stage coarse-crystalline calcite unrelated to ore occurrences reflect deep, downward circulation of river waters from the nearby Brazilian Shield. Further petrographic and fluid inclusion investigations may resolve this question.

BRINE MIGRATION AND FORMATION OF MISSISSIPPI VALLEY-TYPE DEPOSITS

Replacement dolomite, limestone and late-stage carbonates with high $^{87}Sr/^{86}Sr$ ratios, anomalous for Upper Triassic to Lower Jurassic marine carbonates, are commonly restricted to the lower 20 m of the Pucará sequence. This indicates that brine-rock interactions were fairly restricted in vertical extent, and (or) that the ^{87}Sr-enriched fluid was gradually buffered by the carbonate rocks as it moved upwards away from the contact with the Mitu Group.

By contrast, the Sr isotopic trend is different at the San Vicente and Shalipayco Zn-Pb MVT deposits located in the eastern Pucará basin. The different ore zones of the San Vicente deposit occur between about 400 and 1300 m above the clastic sedimentary rocks of the lowermost Pucará Group and the Mitu Group. Replacement and sparry dolomite at that deposit yield $^{87}Sr/^{86}Sr$ ratios that are typically higher than coeval Upper Triassic and Lower Jurassic seawater (Fig.2). This suggests that the carbonate rocks in the San Vicente area interacted with ^{87}Sr-enriched brines which most probably migrated over a considerable vertical distance from the lower detrital rocks of the basin to shallower levels of the Pucará Group. At Shalipayco, where the ore-bearing zones are located up to 500 m above the Mitu Group, coarse-crystalline calcite also contains Sr that is considerably more radiogenic than Upper Triassic seawater Sr (Fig.1). Steeply dipping faults are conceivable channelways for extensive brine ascent from depth in the eastern Pucará basin. Previous studies on MVT deposits have already stressed the importance of faults as favorable channelways to move warm metal-bearing brines from regional aquifers to the site of ore deposition (Pelissonnier 1967, Clendenin and Duane 1990).

The isotopic data of the carbonate host rocks and late stage carbonate cements of the San Vicente Zn-Pb mine display a coherent trend with that of the different carbonate generations sampled regionally in the Pucará basin (Fig.2). This indicates that formation of MVT deposits in the Pucará basin is an integral part of the diagenetic evolution of the basin. Moreover, the isotope data imply a relative late timing for the formation of MVT ore deposits and occurrences during diagenetic evolution.

CONCLUSIONS

1) The combined Sr-O-C isotopic data of the carbonates from the different subsequent evolution stages of the Pucará basin are identical to other studies carried out on burial diagenesis and MVT deposits, where ^{87}Sr/^{86}Sr ratios increase, and δ^{13}C and δ^{18}O values become lighter with the diagenetic paragenetic sequence (e.g. Kesler et al. 1988; Ravenhurst et al. 1989; Kaufman et al. 1990,1991; Mountjoy et al. 1992).
2) The diagenetic evolution of the Pucará basin is similar to that of sedimentary basins in the central United States and western Canada (e.g. Banner et al. 1988; Kaufman et al. 1990, 1991; Mountjoy et al. 1992).
3) The formation of MVT deposits is an integral part of the diagenetic evolution of the Pucará basin and took place at late diagenetic stages.
4) The Sr isotopic data indicate that the carbonate host rocks in the vicinity of MVT deposits interacted with ^{87}Sr-enriched brines which most probably migrated over a considerable vertical distance from the base of the Pucará Group, possibly along steeply dipping faults.
5) Replacement dolomite and limestone with high ^{87}Sr/^{86}Sr ratios, anomalous for Upper Triassic to Lower Jurassic marine carbonates, within the Pucará sequence (excluding the lower part of the Chambará Formation) may possibly be used as a guide for the exploration of hidden MVT deposits.

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