

**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen =  
Bulletin suisse de minéralogie et pétrographie

**Band:** 75 (1995)

**Heft:** 2

**Artikel:** Rare earth element patterns in the host and gangue carbonates of the  
San Vicente zinc-lead deposit, Peru

**Autor:** Spangenberg, J. / Fontboté, L.

**DOI:** <https://doi.org/10.5169/seals-57157>

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SHORT COMMUNICATION

## Rare earth element patterns in the host and gangue carbonates of the San Vicente zinc-lead deposit, Peru\*

by J. Spangenberg<sup>1</sup> and L. Fontboté<sup>1</sup>

### Abstract

The rare earth element (REE) composition of the hydrothermal carbonates of the San Vicente Mississippi Valley-type district, hosted in the Triassic-Jurassic dolostones of the Pucará Group (central Peru), were used to constrain the path-way of the ore fluid and changes in the Eh-pH conditions during mineralization. The ore-stage dark replacement dolomite and white sparry dolomite are depleted in REE compared to the host dolomite. They display negative Ce anomalies. These results suggest that the incoming ore fluid was slightly oxidizing and acidic and poor in REE, which implies that the fluid flow was through a main aquifer, likely the detrital units at the base of the basin and had limited interaction with the carbonate host rocks. The alteration of the native organic matter by the incoming fluid provides the local reducing conditions for thermochemical sulfate reduction (and reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ ). The REE enrichment and the positive Eu anomaly of the late-stage vug-filling carbonates indicate that the post-ore "residual" acidic fluid was again oxidizing due to continuous influx of fresh basinal waters.

*Keywords:* REE, Eh-pH condition, carbonates, Zn-Pb ore, San Vicente deposit, Peru.

### Introduction

Rare earth elements (REE) systematics have been used as tracer of precipitation of sediment-hosted Zn-Pb-(F) ores (e.g., GRAF, 1984, 1988; JONES et al., 1991; MÖLLER, 1983, 1991; MÖLLER and MORTEANI, 1983; MÖLLER et al., 1984; SHEPHERD et al., 1982). GRAF (1984) has documented that the altered host dolomite in the Mississippi Valley-type (MVT) district of Viburnum Trend (southeast Missouri) was significantly depleted in light REE (LREE) compared to the unaltered host dolomite. He explained the differences in the REE patterns by interaction of the host rock with LREE depleted ore solutions.

The present communication is part of an extensive geochemical investigation of the gangue carbonates of the San Vicente MVT district hosted in the Upper Triassic – Lower Jurassic Pucará basin, central Peru. It includes C, O and Sr isotopic data, fluid inclusion studies, and geochemical data of the associated organic mat-

ter (SPANGENBERG, 1995; SPANGENBERG et al., 1994, 1995, and in prep.). The San Vicente deposit has an accumulated production and reserves of about 20 million tons ore of 10% Zn and 0.8% Pb (FONTBOTÉ et al., 1995). The Upper Triassic – Lower Jurassic Pucará basin is a carbonate platform at the western margin of the Brazilian Shield developed at the beginning of the Andean cycle (Norian to Toarcian) by marine transgression over clastic sediments and volcanoclastic rocks of the Upper Permian to Lower Triassic Mitu Group (FONTBOTÉ, 1990; ROSAS, 1994). In the San Vicente mining area the carbonate sequence of the Pucará Group has a thickness of about 1300 m (from Norian to Hettangian). Three dolomitic units (San Judas Dolomite, San Vicente Dolomite, Alfonso Dolomite) host the orebodies. The mineralization (sphalerite and subordinate galena) largely replaces dolomitized subtidal oolitic grainstones interlayered with dolomitized mudstones rich in organic matter and bearing evapo-

\* Extended abstract of a contribution presented at the annual meeting of the Swiss Society of Mineralogy and Petrology, Aarau, October, 1994.

<sup>1</sup> Département de Minéralogie, Université de Genève, rue des Maraîchers 13, CH-1211 Genève 4, Switzerland.

ritic sulfate pseudomorphs (sabkha facies). It appears in part as zebra ore and occasionally as cement in breccias or veinlets (FONTBOTÉ and GORZAWSKI, 1990; SPANGENBERG et al., 1995). White sparry dolomite (WSD) is the main hydrothermal gangue carbonate.

FONTBOTÉ and GORZAWSKI (1990) proposed that San Vicente formed at a burial depth of about 2–3 km and a temperature range of about 70 to 160 °C by influx of a metal-bearing saline brine characterized by radiogenic Sr and Pb. Extensive petrographic and isotopic (C, O, Sr, S, and Pb) information is available on the San Vicente main deposit. The results of preliminary fluid inclusion studies indicate that the white sparry dolomite was precipitated from hot (115 to 162 °C) and saline (up to 26 wt% eq. NaCl) fluids (MORITZ et al., in press).

The aim of this contribution is to discuss the constraints set by the REE behavior in the gangue carbonates on the source of the ore solutions, its path-ways, and the processes involved during ore precipitation at San Vicente.

### Sampling and methods

The San Vicente mining area was submitted to an extensive sampling, which include samples at different orebodies from the three ore-bearing dolomitic units and the Uncush bituminous silty Limestone (UL), that overlies the major ore-bearing dolomitic unit (San Vicente Dolomite) and provide a stratigraphic reference. The following carbonate generations were separated using a diamond drill table-press: dark replacement dolomite (DRD, I), white sparry dolomite (WSD, II), late filling dolomite (LFD, III) or calcite (LFC, III), and calcite replacing evaporitic sulfate (EPC). On the basis of fabric, preservation of primary texture, and grain size criteria we have distinguished three subgenerations of DRD, which present different degree of hydrothermal alteration. They are: "Ivf" very fine-grained, "If" fine-grained, and "Im" medium-grained.

The different carbonate generations were analyzed for rare earth elements by ICP-MS (1N HCl-digestion).

### Results and discussion

The distribution of the REE content in the different carbonate generations is illustrated in figure 1.

The bituminous silty Uncush limestone shows the highest REE concentration ( $\Sigma$ REE about

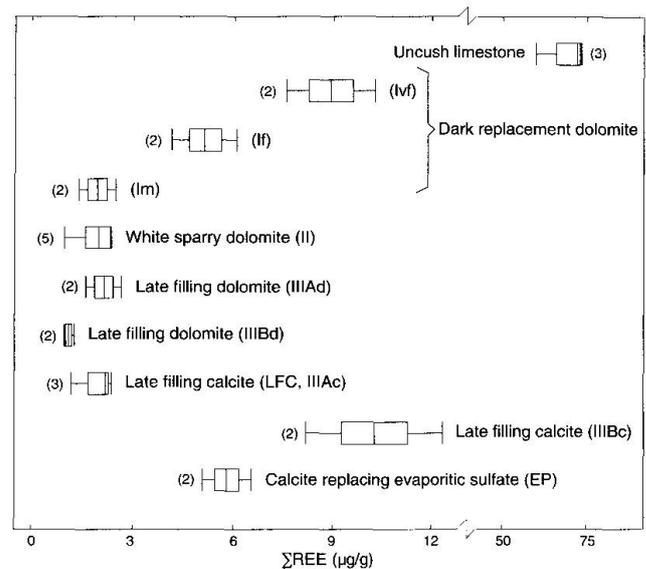


Fig. 1 Ranges and medians of the total rare earth element abundance of the carbonates from San Vicente deposit. UL = bituminous silty Uncush limestone; DRD = dark replacement dolomite ("Ivf" very fine-grained, "If" fine-grained, "Im" medium grained); WSD = white sparry dolomite (II); LFD = late filling dolomite (IIIAd and IIIBd); LFC = late filling calcite (IIIAc and IIIBc); EPC = calcite replacing evaporitic sulfate.

72  $\mu\text{g/g}$ ). In the other carbonate phases the REE content is lower than 12  $\mu\text{g/g}$ . The concentration of REE in the ore stage dolomites decreases from the host DRD to the WSD (Ivf: 8.9  $\mu\text{g/g}$ ; If: 5.0  $\mu\text{g/g}$ ; Im: 1.8  $\mu\text{g/g}$ ; II: 1.8  $\mu\text{g/g}$ ). The late filling carbonates show a large range of REE contents (LFD: 0.9 to 2.5  $\mu\text{g/g}$ ; LFC: 1.2 to 12.4  $\mu\text{g/g}$ ), which correlates with textural and paragenetic features. In order to discuss this broad range the late carbonates were subdivided as follows. Late filling dolomites (IIIAd and IIIBd) occur in barren and sphalerite-bearing cements, respectively, of hydraulic breccias. Calcites "IIIAc" are translucent filling of voids in dissolution porosity, and "IIIBc" white calcites fill large vein-like open spaces in hydraulic breccias. The dolomites have a similar REE content (IIIAd: 1.5 to 2.5  $\mu\text{g/g}$ ; IIIBd: 0.9 to 1.2  $\mu\text{g/g}$ ) but different REE patterns, whereas the calcites differ in the REE abundance (IIIAc: 1.2 to 2.2  $\mu\text{g/g}$ ; IIIBc: 8.3 to 12.2  $\mu\text{g/g}$ ) and patterns (see below).

The REE patterns of the very fine-grained dark replacement dolomite (Ivf) are shaped similarly to those of the Uncush limestone (Fig. 2). This suggests, that the bituminous silty Uncush limestone and the host dolomite inherited its REE patterns from Jurassic seawater and marine pore-water. The most significant feature of the REE distribution in the subgenerations of the

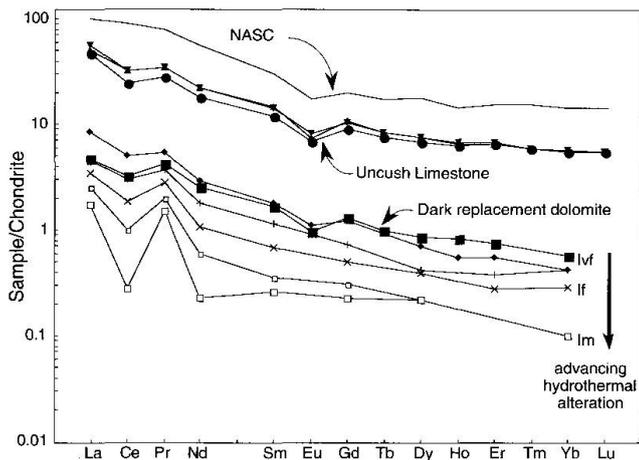


Fig. 2 Chondrite-normalized REE abundances in Uncush limestone and subgenerations of dark replacement dolomite (DRD) from the San Vicente deposit. Compare to North American shale composite (NASC). The REE patterns of the hostdolomite (Ivf) are similar in the different ore-bearing dolomite units ( Alfonso Dolomite, San Vicente Dolomite, San Judas Dolomite).

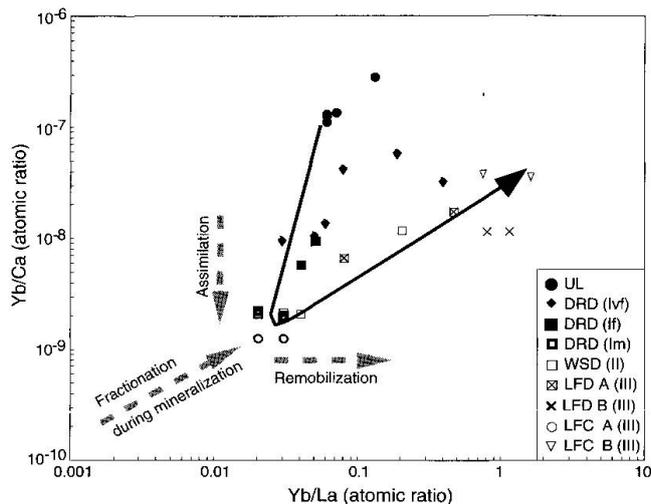


Fig. 4 Yb/Ca versus Yb/La plot of the hydrothermal carbonates in the San Vicente deposit showing the trends of REE fractionation during mineralization defined by PAREKH and MÖLLER (1977). Abbreviations as in figure 1.

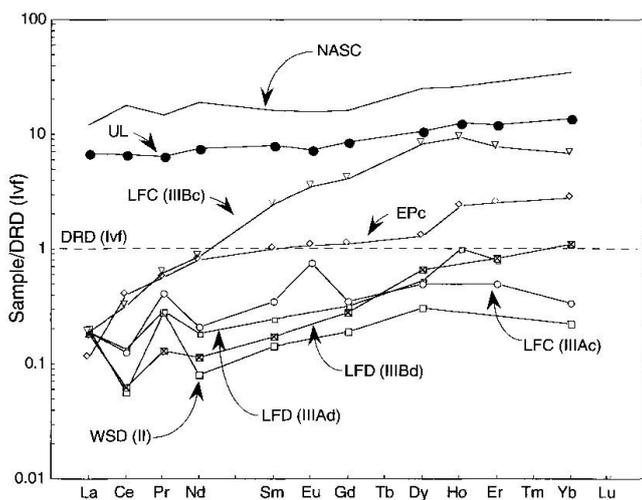


Fig. 3 Median REE patterns of the Uncush limestone, and the hydrothermal carbonates normalized to the very fine replacement dolomite (DRD, Ivf). Abbreviations as in figure 1.

DRD is a systematic depletion in Ce and generally, less pronounced, of all the REE, with advancing hydrothermal alteration (Fig. 2).

The REE spectra normalized to the average host dolomite (Ivf) show significant trends (Fig. 3): (1) all the hydrothermal carbonates are markedly depleted in LREE compared to HREE; (2) the ore-stage dolomite (WSD, LFD) shows pronounced negative Ce anomalies, suggesting that the incoming ore fluid was depleted in LREE, and particularly in Ce; (3) late filling calcite intergrown with late sphalerite cementing dissolution breccias (III Ac) is depleted in LREE but has a

positive Eu anomaly ( $Eu/Eu^* = 2.6$ ); (4) the LFC from a large vein in the hydraulic breccia (III Bc) shows a pronounced enrichment in MREE and HREE. Furthermore, the extensive depletion of the ore-stage dolomites compared to the host dolomite indicate that no compositional resetting (REE enrichment) took place between the ore fluid and the REE-rich Uncush limestone. This is consistent with the stable isotope evidence against considering the bituminous silty Uncush Limestone as a source or channel-pathway of the ore fluid (SPANGENBERG, 1995).

The overall fractionation of the REE in hydrothermal carbonates can be explained in the Yb/Ca versus Yb/La space, according to PAREKH and MÖLLER (1977), in terms of *assimilation* and *remobilization* during mineralization (Fig. 4). The vertical (Yb/Ca ratio) component indicates the extent of interaction (*assimilation*) between the host dolomite and the fluid during increasing water-rock ratios, while the horizontal (Yb/La ratio) the overall REE-fractionation (*remobilization*).

The hydrothermal carbonates (DRD, WSD, LFD, and LFC) of San Vicente display a roughly diagonal trend in the Yb/Ca–Yb/La diagram (Fig. 4), indicating that they were precipitated from a fluid whose REE fractionation increases during mineralization. The important horizontal component (Yb/La) to the overall trend suggests that the ore fluid was complexing controlled.  $CO_2$  partial pressure and pH control the stability of the hard REE- $CO_3^{2-}$  complexes. Thus, the precipitation of sulfides, which acidifies the ore solu-

tion, and CO<sub>2</sub> degassing due to an enhanced hydrothermal porosity, would cause the precipitation of REE-rich late carbonates.

The pronounced depletion in LREE, and scatter in REE patterns of the ore-stage dolomites (altered DRD, WSD) of San Vicente deposit reflects alteration of the host dolomite (very fine-grained DRD) by circulation of large amount of REE-poor solutions. McLENNAN (1989) states that, in contrast to other trace elements (such as Sr), extremely high fluid-rock ratios (e.g., F/R > 10<sup>3</sup>) are required to modify the REE concentration of carbonates during diagenetic processes. The MREE and HREE enrichment of the late open-space filling carbonates (III) suggests that these carbonates precipitated in a fluid-buffered system. This enrichment in REE may be due to changes of pH and Eh. We conclude that the incoming mineralizing fluid (REE-poor) was not in chemical equilibrium with the carbonates of the Pucará Group. The same conclusion is attained through stable isotope data (SPANGENBERG et al., 1994; SPANGENBERG, 1995). This implies that the fluid flow was through a main aquifer, likely the detrital units at the base of the basin, without or with little interaction with the Pucará carbonates. Access to the ore sites was by interconnected channel-ways (faults, basement highs) near the ore occurrences.

### Summary and conclusions

The negative Ce anomaly in the ore-stage dolomite of the San Vicente deposit (Figs 2–3) supports early (pre-ore) circulation of the incoming fluid in oxidizing environment, in which Ce was depleted compared to the neighboring La and Pr.

The positive Eu anomalies of the late calcites indicate that the fluid was enriched in the (mobile) Eu<sup>+2</sup> (e.g. SVERJENSKY, 1984) during the main-mineralization stage; afterwards oxidized to Eu<sup>+3</sup> which precipitated with the post-ore carbonates. Thus, the Eu anomalies (and the Fe–Mn covariations, SPANGENBERG, 1995) of the hydrothermal carbonates record the change from reducing ore-stage to post-ore oxidizing conditions. These changes of the Eh-pH conditions of the ore fluid are interpreted to be due to mixing of the native intra-formational fluid (alkaline, reducing, HCO<sub>3</sub><sup>-</sup> dominant) with the incoming mineralizing fluid (slightly acidic, oxidizing, H<sub>2</sub>CO<sub>3</sub> dominant) in an open dynamic system.

The negative Ce anomaly in the ore-stage dolomite suggest that the incoming ore fluid was slightly oxidizing. This is consistent with its early

(pre-ore) migration along an oxidizing main aquifer, such as the red sandstones and other clastic units at the base of the basin.

Ore precipitation decreases fluid pH and destabilizes REE-complexes. Thus more evolved fluid enriched in uncomplexed heavy REE precipitates late filling calcites. This enrichment in REE and the positive Eu anomaly may be due to changes of pH and Eh during the mineralizing events in San Vicente.

Alteration of the organic matter disseminated in the host dolomite by the incoming ore fluid liberated hydrocarbons which locally produced reducing conditions that led to the thermochemical reduction of sulfate (SPANGENBERG, 1995) and the reduction of Eu<sup>+3</sup> to Eu<sup>+2</sup>.

### Acknowledgements

This study is supported by the Swiss National Science Foundation (Grant No. 20.36397.92). We are grateful to San Ignacio de Morococha S.A. Mining Company and the staff of the Geology Department of San Vicente mine for their help in the field work. The authors thank Ph. Thélin of the University of Lausanne for their cooperation during the XRD-analyses.

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Manuscript accepted April 19, 1995.