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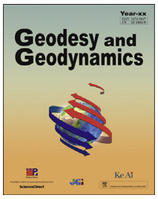

Establishing geothermometric constraints on the local geothermal gradients: Case study of the Eastern Cordillera Basin, Colombia

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Geochemical analyses were performed on 170 coal bed-trapped groundwater samples from 97 underground mines located in the Eastern Cordillera Basin, Colombia. The waters analyzed in this paper are from exploited coal beds, located up to 0.73 km deep, which emerge along with the local fault systems. The hydrochemical facies were classified based on the concentration of major ions by inferring the equilibrium state and rock water source. The main hydrochemical facies presented in the groundwater study are SO_4–Ca–Mg, HCO_3–Ca, HCO_3–Ca–Mg, and SO_4–HCO_3 mixed waters. We used geothermometric equations to estimate the most probable temperature under in-situ conditions and the propagation of errors theory to test the results. The geothermal gradient in the study area is close to 30 °C/km, which is consistent with measurements from oil wells within the study area. A Principal Component Analysis was used to explain factors affecting formation water composition and hydrogeochemical evolution of aquifers.

Q2 1. Introduction

Geothermics is a broad discipline in geophysics that deals with the theoretical study of the thermal regimes in the Earth, as well as engineering aspects using the Earth's natural heat. A relevant thermophysical parameter in this discipline is the geothermal gradient. This key piece of information is essential in the understanding of the thermal lithospheric structure and the thermal history of sedimentary basins, allowing for the evaluation of organic matter maturity and the generation of hydrocarbons. Also, it can be used to study the geothermal resources in a particular region. A widely used approach for geothermal gradient estimation is made by analyzing geochemical thermometers, which are empirical relations that correlate ion concentrations and temperatures at depths, and are based on the chemical balance between groundwater and local lithology [1,2]. However, in a sedimentary basin setting, geochemical thermometers are only applicable to scenarios where the pore water remains in a chemical equilibrium with the surrounding rocks, subject to in-situ temperature conditions.

There are gaps in knowledge regarding the behavior of these techniques when it comes to inferring the thermal structure of sedimentary basins which coexist with coal ore deposits, salt domes, and complex tectonic structures with current levels of orogenic activity. In this paper, we analyze the hydrogeological components and their relationship with the stratigraphic units of the Eastern Cordillera Basin in Colombia, in order to map thermal anomalies, and compare the results with well observations. We have estimated temperatures using chemical geothermometer, and have selected them on the basis of the propagation of errors theory. Consequently, the geothermal gradient is derived from the local stratigraphic record. The hydrogeochemical data has been used to generate maps and identify trends in the concentrations of Na, Ca, K, Mg, SO_4, HCO_3, CO_3, and Cl. Finally, a multivariate analysis was performed to evaluate the behavior of temperature as a function of the chemical components of the geothermometers used.

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2. Geological setting

The Eastern Cordillera Basin (ECB) in Colombia constitutes rocks formed in an inverted Late Triassic rift system following the break-up of Pangea [3], that are overlain] by Mesozoic marine and Cenozoic continental sediments. Since the Early Paleogene, a dextral transpressional deformation, related to the Andean Orogeny, promoted the current structural inversion of the basin, with high thermal anomalies associated with the hydrothermal activity [4]. Coal beds in the basin are associated with the Guaduas Formation [5], that were deposited in a transitional environment during the Late Cretaceous to Early Paleocene. Previous studies have described the stratigraphy of this unit as a mainly muddy succession with some sandy levels, characterized by containing several layers of coal [6].

Fig. 1 shows the study area, located west of the Eastern Cordillera Basin, Colombia. The structures in the area are dominated by the Cucunubá, Chital, and Choconta Faults. These are reverse faults with orientated mainly in the NE direction [7]. Here, the coal beds occur in the Guaduas Formation, which were deposited in a coastal wetland and floodplain environment [8]. Fig. 2 shows the lithostratigraphic column of the Eastern Cordillera Basin. Several authors have described the geology and hydrogeology of the study area [7,9–13]. The Guaduas Formation comprises beds of claystone, coals, and sandstones. Palynological studies assign the Guaduas Formation to the Upper Maastrichtian-Lower Paleocene age [14]. In the study area, the Guaduas Formation is about 200 m thick [15].

Previous studies in the area have classified the coal as a high volatile bituminous A-type, in accordance with the Standard Classification of Coals, Rank ASTM D-388. The coals in this formation are dominated by macerals of the vitrinite group, with a lesser contribution of the inertinite and exinite groups. The mineral fraction corresponds to pyrite and clays minerals [16].

Other units in the area (Fig. 2) correspond to rocks of the Hilo Formation, a rock complex that includes shales, biomicrites, and diagenetic cherts that resulted from the replacement of biomicrite by silica [17,18]. Overlying this unit is the Pacho Formation, which constitutes mudstones and siltstones, with sporadic interbedding of sandstones, and a few horizons of grainstone/rudstone biosparites, and sandy biosparites [19]. Caceres and Etayo [20] defined the Frontera Formation to the Turonian strata composed of shales with calcareous concretions and beds of biomicrite, including thin beds of porcellanites and biogenic cherts. The Conejo Formation is made of mudstones and marlstones, with large Coniacian to Santonian calcareous concretions and minor biomicrite and sandstone interbeds. The overlying Arenisca Dura Formation is a Campanian quartz sandstone of medium fine-grained and sandy mudstones. The Plaeners Formation [21,22] includes "siliceous" siltstones and claystone, along with "lidites" and "porcellanites" fractured in cubic silica prisms. The unit includes phosphatic particles, fish spines and teeth, mud intraclasts, bioturbated strata and calcareous concretions with abundant pyrite and some ichnofossils [23]. The Labor Tierna Formation is usually used to group sandstones of fine-medium grained with occasional interleaves of mudstones layers with glauconitic and phosphate particles, and fish parts. The Labor Tierna Formation [21] is composed of medium to coarse-grained quartz sandstones. Using thin section analysis, Perez and Salazar [10] described the rocks as muddy sandstones of very fine to fine-grain size.

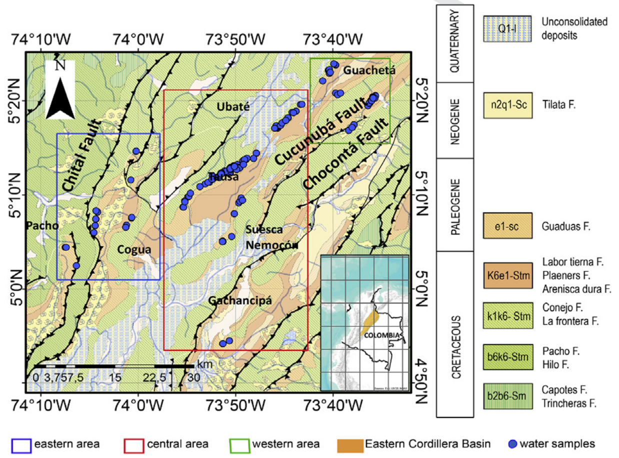

Fig. 1. Geological setting of the Eastern Cordillera Basin, showing the major faults (indented black lines) and stratigraphic units. The blue circles represent locations sampled for the groundwater analyzed in this study, that are related to coal mines. The boxes indicate the three geographical areas where groundwater samples were collected. Geological units outcropping in the area correspond to sedimentary sequences of the Cretaceous to Quaternary period.

3. Methodology

One hundred and seventy groundwater samples were collected around the coal mines located in the Eastern Cordillera Basin between December 2014 and April 2015 (ANH-Antek S.A.S, [24]). In-situ parameters including temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were analyzed using a properly calibrated multi-parametric Hach D-660 instrument.

A 500 mL water sample was collected for major cation and metal analyses, and acidified to pH < 2 using ultra-pure concentrated nitric acid. The Antek S.A.S-Environmental and Geochemical Laboratory ran all analyses including total and suspended solids, alkalinity, chloride, total calcium and magnesium hardness, carbonate, and bicarbonate, which were analyzed using gravimetric and titrimetric validation methods [25] based on U.S. EPA and Standard Methods (APHA/AWWA/WEF, [26]). Sulfates were analyzed using a Thermo Scientific Spectrophotometer. The cations and major elements such as calcium, magnesium, sodium, potassium, and iron, were analyzed using a Perkin–Elmer 800 Atomic Absorption Spectrometer. The analytical precision, based on the ionic balance error, was <10% [27,28].

The Aquachem 5.1 hydrogeochemical software, version 2007–2008 from Waterloo Hydrogeologic [29] was used for the determination of geochemical correlations, graphics, ionic balance, dissolved minerals and other hydrogeochemical parameters. Concentration maps were modeled using the ArcGis-10.2 software (ESRI Inc., [30]). A Multivariate Statistical Analysis was done using the XLStat software [31]. A Principal Component Analysis was used to explain the relationship between numerous variables, and establish the factors affecting formation water composition. The geothermeters were calculated based on concentrations of major ions (mg/l) using the SolGeo tool developed by Verma et al. [32]. A cluster analysis was carried out to investigate the similarities in each of the major ion concentrations using the median as the central measurement criterion (due to the asymmetrical probability function) [33,34].

The estimation of geothermometers requires a proper depth selection in the study area which guarantees a suitable fit for the current geological setting. Temperature estimations were derived from empirical relationships presented in Table 2. Concentrations in meq/L were converted to mg/l and replaced in these equations. We used previously reported relations as criterium for the selecting the best relation between ions and temperatures [1,35] based on the propagation of errors theory [36]. These mathematical relations were applied to the geothermometers using the variance provided with the original data used by authors to develop the equations relating to the analytical errors (see equations in Appendix A). For calculation of the geothermal gradient, we compared depths reported from the coal mines, where in-situ groundwater samples were collected, structural approximations made by previous

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