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Determination of Geochemical Correlation of Cu, Pb, Zn in Stream Sediment Samples in Barru Area, South Sulawesi

3

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Determination of Geochemical Correlation of Cu, Pb, Zn in Stream Sediment Samples in Barru Area, South Sulawesi

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Abstract. The Barru area is known as the rock basement location in Sulawesi Island. The disclosure of ultramafic rock, metamorphic rock, and various sedimentary rock formations in the field and outcrops of unmapping intrusive rocks on a regional scale are certainly very interesting to be used as a media experiment in statistical methods in exploration of mineral resources. This is quite reasonable because among these rock formations are revealed intrusion of dacite and diorite rocks which are altered and deposited as sulfides. The research gradually combines the pearson hybrid correlation geochemical stream sediment data and intrusive rocks on the relationship between SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, and Cr₂O₃ variables which are illustrated by multidimensional spatial correspondence analysis and anomalous sources based on Cr, Cu, Fe, Mn, Ni, Zn, As, Mo, Co, Sb, Cd, and Pb variables. The results showed that the application of the hybrid statistical analysis method was effective enough to identify elemental variables in identifying sulfide deposits and the characteristics of anomalies were quite different from diorite and dacite due to magmatic hydrothermal and tectonic activity.

1. Introduction


Stream sediment is a simple method of taking samples of various small sizes that form naturally [1]. Initially, this method was very popular in the mineral exploration in reconnaissance stage in the tropics and sub-tropics. is currently used in environmental research mainly in lake and river sedimentary materials.

Regionally, study area is occupied by complex metamorphic rocks and ultramafic rocks which form the basement rocks of Sulawesi Island [2]. Various sedimentary rock formations, intrusion of dacite, diorite and there are still some unmapping mineralized intrusive rocks. Reflections on the complex differences in the rocks cause various types of river genetically such as consequent, insequent and subsequent rivers, which are generally divided into two directions, namely flowing to north and south through various rock formations. Flow effects affect in elemental transportation [3, 4] and it is mainly associated with the formation of river deposit.

Statistics and stream sediment are a solid combination method following the elemental mobility properties that can be used as univariate or multivariate analysis, that is aiming to evaluate the geochemical variables [5], one of which is pearson correlation. The research applies multivariate pearson correlation to evaluate the strong variables between existing elements, ultimately facilitating the analysis of spatial mapping factors between elements.

The research location was chosen which was easily accessed from the highway, to investigate the dispersion characteristics of various elements and indications of the type of metal sulfide deposits. The



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research also evaluated the effectiveness of random sampling techniques based on river flow through various types of rock formations.

2. Regional Geology ¹

The stratigraphy of the study area is included in the Geological Map of the Pangkajene and Western Watampone Sheets [6], namely (Figure 1):

s: Metamorf Complex; schist, gneiss, glaucophane, garnet, epidote, muscovite, chlorite, eclogite, garnet schist, amphibole schist, chlorite schist, muscovite schist, muscovite-tremolite-actinolite schist. It generally spreads to the Northeast, rising up by fault towards the Southwest.

Ub: Ultramafic Rocks; peridotite, serpentinite, contains chromite lenses and laterite.

m: Melange Complex; graywacke, breccia, conglomerate, sandstone, gray shale, red shale, red radiolarian chert, slate, schist, ultramafic rock, basalt, diorite, and mudstone.

Kb: Balangbaru Formation; flysch-sediment types; sandstone siltstone-intercalated, claystone and shale; intercalated conglomerates, tuffs and lava; the sandstones are composed of graywacke, arkose, tuff and carbonate rock, conglomerates with basalt, andesite, diorite, shale, splattered tuff, schist, quartz, and cemented by sandstone. This formation is overlapped by Mallawa Formation and prophylic volcanic rocks which are composite and unconformable with the Bantimala tectonic complex.

Tem: Mallawa Formation; sandstones, conglomerates, siltstone, claystone, marl with coal lenses or beds and claystone intercalation; the sandstones are mostly quartz sandstones, and there are also arkose, graywacke, and tuffaceous rocks. It is conformable with the Tem limestone and that unconformable with Kb sedimentary rocks and Tpv volcanic rocks.

Temt: Tonasa Formation; massive coral limestone, bioclastic limestone and calcarenite, bituminous limestone. It is unconformable with Mallawa Formation and Camba Formation, intruded by sill, dyke, and igneous rock stocks which are basal, trachyte and diorite.

Tmcv: Member of Volcanic Rocks Camba Formation; volcanic rocks are intercalated by marine sedimentary rocks; volcanic breccia, lava, volcanic conglomerates, fine grained to lapilli tuff; intercalated tuffaceous sandstones, carbonate sandstones and mudstones. It is intruded by dykes, sills, and stock of basalt and diorite arrangements, andesitic-basaltic tuffs, andesites, andesitic trachyte, and leusite basalt.

d: diorite – granodiorite; diorite intrusion, granodiorite, mainly in the form of stock, and partly in the form of dykes, mostly in porphyry textures, light gray to gray colour. Diorite, that is exposed to the east of Barru, intrudes the sandstone of the Balangbaru Formation. Ultramafic rock, porphyry granodiorite, with many of biotite-amphibole phenocrysts, and it intrudes Tonasa Formation's limestone and Camba Formation.

3. Methods

Random sampling of sediments and water acidity is carried out on rivers that pass through rock formations, namely Watu River, Palakka River, Pijae River, Barru River. Water acidity is measured in the field and rock samples are taken as comparative correlation controllers.

Data distribution is considered to represent the distribution of rock formations which is divided into four groups: (1) SS02, Balangbaru Formation, Tonasa Formation, Tonasa Formation, Metamorphic Complex (2) SS01, SS03 and SS04: Tonasa Formation (3) SS05, SS06 and SS07: Tonasa Formation, Camba Formation, Ultramafic Complex (4) SS08, SS09: Tonasa Formation, Camba Formation, diorite intrusion. Data on SS02, SS08, SS09 are considered to be single correlated statistics as independent factors.

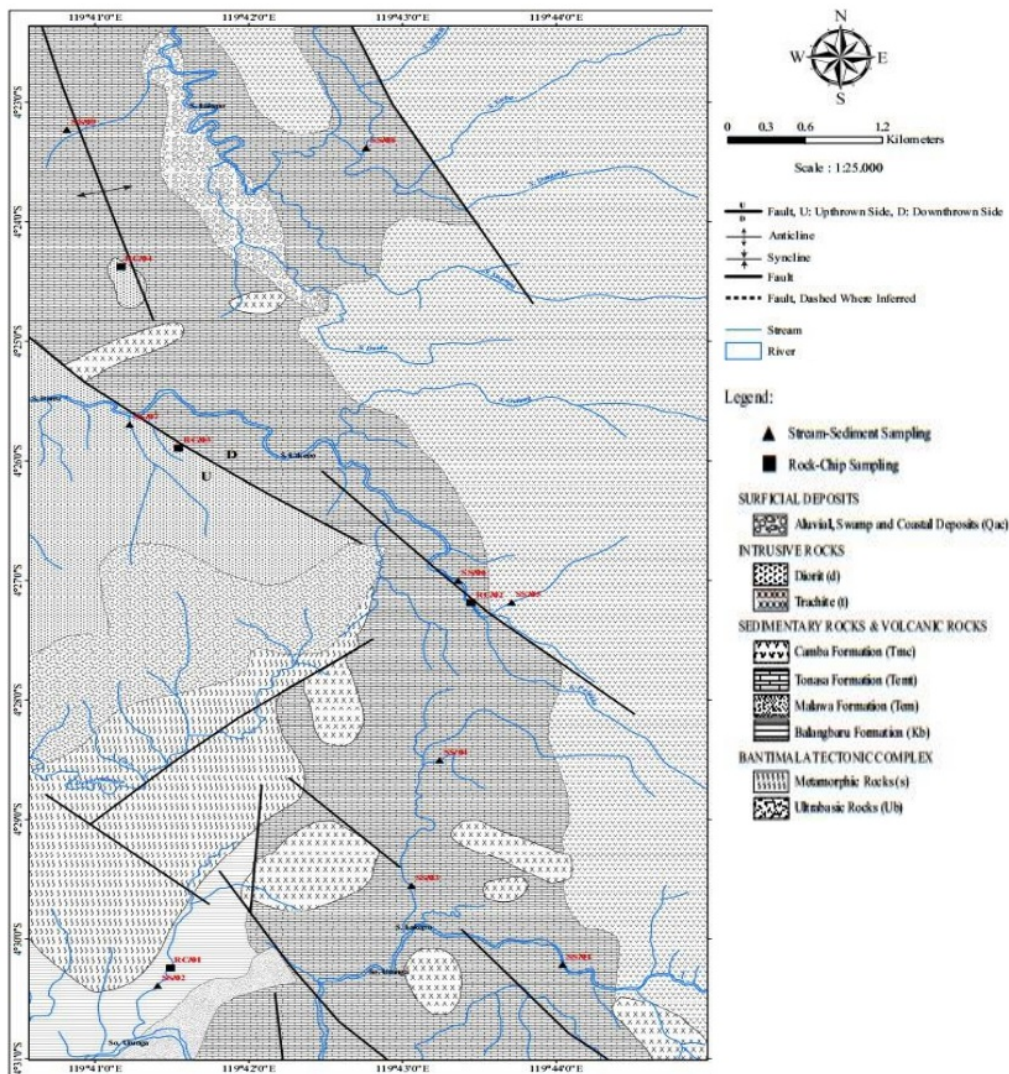


Figure 1. Regional Geology and sampling point

Taking of fresh dacite (RC01) and (RC04), diorite alteration (RC02), and dacite alteration (RC03) samples are used as a major linearity element, then composite river sediment samples at each creek on different trajectories are randomly collected from the bottom in 20 to 30 cm depth of active flow channel by using a shovel.

The samples are homogenized and that is washed by the wood pan. The panning or washing process is carried out under the surface of the water repeatedly to separate heavy particles and clays which produce heavy mineral residues. Then, the concentrate was dried in air before being submitted for XRF chemical analysis and ICP-MS analysis in Intertek Jakarta for find the value of Al_2O_3 , Fe_2O_3 , MnO , SiO_2 , CaO , K_2O , Na_2O , TiO_2 , Cr_2O_3 , MgO , P_2O_5 , S dan Cu, Pb, Zn, As, Fe, and Cr.

Laboratory data is converted into a standard format in the Excel database, statistics on the IBM SPSS 25 and geochemical information which is obtained by maps created using ArcGIS 10.3 software.

4. Result and Discussion

4.1. Rocks Geochemistry

Statistical description of the chemical samples of rock RC01, RC02, RC03, RC04 show the maximum and minimum range of major elements as follows: SiO₂ (29.36% -83.78%), TiO₂ (0.07% -0.23%), Al₂O₃ (2.97% -6.96%), F₂O₃ (1.88% -8.11%), MnO (0.02% -0.23%), MgO (0.32% -1.32%), CaO (0.02% -29.33%), Na₂O (0.04% -5.37%), K₂O (0.09% -2.02%), P₂O₅ (0.02% -0.10%), Cr₂O₃ (0.0% -1.0%).

The value of SiO₂ is high enough which strengthens the interpretation that river sediment material originates from alteration of dacite and diorite rocks, although contamination can be occurred by quartz sand sedimentation of the Tonasa Formation.

Scatterplot analysis of SiO₂ variables in rock samples that have showed a strong correlation can be found in altered-sulfide mineralized dacite and diorite (Figure 2).

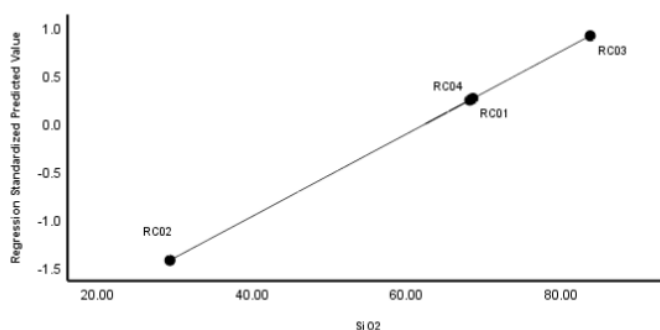


Figure 2. Scatterplot of rock point

4.2. Element Correlation

River sediment material is sourced from rock masses undergoing weathering and transportation processes which subsequently serve as guidelines in identifying source and deposit correlations. Stream sediments generally reflect the mineralogical composition and the presence of outcrops in the drainagebasin, upstream of the sampling sites [1]. Descriptions on stream sediment samples on major elements can be seen in Table 1.

Table 1. Major elements of stream sediment samples

| ELEMENT(%) | SS01 | SS02 | SS03 | SS05 | SS06 | SS07 | DET LIMIT |
|--------------------------------|-------|-------|-------|-------|-------|-------|-----------|
| SiO ₂ | 39.40 | 82.68 | 41.45 | 45.82 | 46.75 | 49.18 | 0.01 |
| TiO ₂ | 1.78 | 1.70 | 1.66 | 1.22 | 1.09 | 1.29 | 0.01 |
| Al ₂ O ₃ | 5.00 | 4.54 | 4.41 | 6.09 | 8.46 | 8.72 | 0.01 |
| Fe ₂ O ₃ | 20.58 | 7.06 | 18.60 | 14.40 | 13.11 | 14.28 | 0.01 |
| MnO | 0.25 | 0.08 | 0.24 | 0.22 | 0.20 | 0.22 | 0.01 |
| MgO | 10.65 | 0.70 | 11.98 | 10.88 | 8.71 | 7.70 | 0.01 |
| CaO | 18.58 | 0.70 | 19.63 | 17.49 | 14.62 | 12.53 | 0.01 |
| Na ₂ O | 0.45 | 0.43 | 0.38 | 0.72 | 0.94 | 1.04 | 0.01 |
| K ₂ O | 0.55 | 0.62 | 0.27 | 1.20 | 2.05 | 2.06 | 0.01 |
| P ₂ O ₅ | 0.34 | 0.04 | 0.31 | 0.33 | 0.36 | 0.36 | 0.01 |
| Cr ₂ O ₃ | 0.07 | 0.28 | 0.01 | 0.08 | 0.05 | 0.05 | 0.01 |
| S | 0.02 | 0.01 | 0.01 | 0.02 | 0.03 | 0.02 | 0.01 |
| LOI | 2.20 | 1.00 | 1.10 | 1.90 | 3.10 | 2.20 | 0.01 |

Pearson correlation uses 0.5 as a measure of the major element variables in SS01 / SS02 / SS03 data group and SS05/06/07 data group. The results are known that are three groups and strongly correlated each others: (1) $(Al_2O_3, K_2O) = (0.99) = (Al_2O_3, K_2O) = 0.99$; $(Al_2O_3, Na_2O) = 0.82 < (Al_2O_3, Na_2O) = 0.98$; $(Al_2O_3, P_2O_5) = 0.74 < (Al_2O_3, P_2O_5) = 0.97$; $(Cr_2O_3, Fe_2O_3) = 0.81 > (Cr_2O_3, Fe_2O_3) = 0.70$; $(Cr_2O_3, MnO) = 0.93 > (Al_2O_3, MnO) = 0.70$, (2) $(Cr_2O_3, TiO_2) = 0.99$; $(Cr_2O_3, S) = 0.99$; $(Fe_2O_3, MnO) = 0.97$; $(Cr_2O_3, S) = 0.90$; $(SiO_2, CaO) = 0.80$ $(SiO_2, MgO) = 0.99$; $(Na_2O, Al_2O_3) = 0.82$; $(Na_2O, P_2O_5) = 0.99$, (3) $(Al_2O_3, SiO_2) = 0.80$; $(Cr_2O_3, MgO) = 0.90$; $(Fe_2O_3, TiO_2) = 0.90$; $(K_2O, SiO_2) = 0.72$; $(K_2O, S) = 0.84$; $(P_2O_5, Al_2O_3) = 0.97$; $(K_2O, TiO_2) = 0.97$, $(MgO, CaO) = 0.99$; $(MgO, Cr_2O_3) = 0.88$.

Figure 3, multidimensional and correlation spatial maps show that euclidian distance CaO, Na₂O, MgO have similar distances and close to each other compared to Al₂O₃, then P₂O₅ and SiO₂ respectively in different quadrants. The position of SiO₂ and P₂O₅ in different quadrants and Cr₂O₃, Fe₂O₃ and MnO are in the same quadrant even though Cr₂O₃ is closer to Fe₂O₃ than MnO.

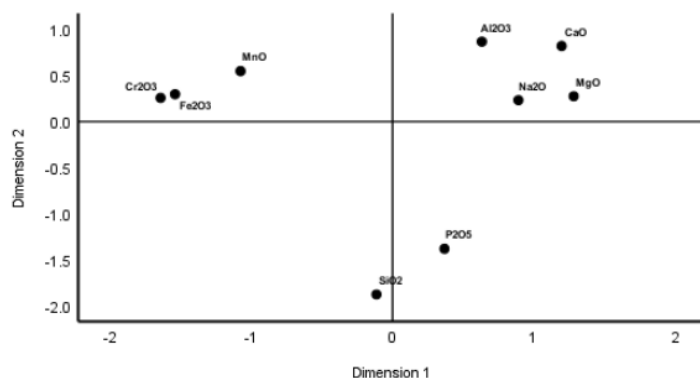


Figure 3. Spatial map of major elements

Statistic analysis in SS01 and SS08/09 as follows : Fe (5.07 ppm) < Fe (mean 22.5 ppm), Cr (1740 ppm) < Cr (mean 1201 ppm), Ni (27 ppm) < Ni (mean 89.5 ppm), Co (12 ppm) < Co (mean 96.5 ppm), Mn (631 ppm) < Mn (mean 6820 ppm). This difference is influenced by weathering of ultramafic rocks which produce ferromagnesian material in river deposits.

The present of mineralized dacite intrusion which is in contact with ultramafic and mineralized diorite in contact with limestone is characterized by an elemental contents: Cu (12 ppm) < Cu (mean 56.5 ppm), Pb (9.0 ppm) < Pb (mean 31.5 ppm), Zn (65 ppm) < Zn (mean 256 ppm), Mo (0.6 ppm) < Mo (mean 1.3 ppm), As (4.0 ppm) < As (mean 21 ppm) and Sb (0.4 ppm) < Sb (mean 1.35 ppm).

By using a 0.5 correlation in the sample group, we obtain six classifications of elemental properties, as follows:

- (1) Equal strong correlation : Fe, Cr, Co, Ni, As, Cu, Pb, Mo, Sb, Cd, Zn, Mo, Mn
- (2) Strong correlation : Zn, Pb, As
- (3) Inverse Correlation : Fe, Cr, Ni, As, Zn, Pb, Co, Cu, Mn
- (4) Without correlation : (Cr, Co), (As, Sb), (Cd, Pb), (Fe, Mn), (Fe, Mo), (Fe, Sb), (Fe, Mo), (Fe, As), (Fe, Cd), (Cu, Fe), (Cu, Mn), (Cr, Sb), (Cr, Fe), (Cr, Mn), (Mn, Sb), (Ni, As), (Ni, Sb), (Zn, Fe), (Zn, Sb), (Mo, Mn), (Mo, Fe), (Sb, Cr), (Sb, Ni), (Sb, Zn), (Cu, As), (Cu, Sb), (Cu, Cr), (Ni, Co), (Zn, Co), (As, Cu), (As, Cd), (As, Co), (Cd, Zn), (Cd, Mo), (Cd, Pb), (Co, As), (Mo, Cd), (Mo, As), (Sb, Cu), (Sb, Cd), (Sb, Cu) (Table 2).

Table 2. Pearson correlation trace elements

| | Cr | Cu | Fe | Mn | Ni | Zn | As | Mo | Co | Sb | Cd | Pb |
|----|------|------|----|------|------|----|------|------|----|----|-----|-----|
| Cr | | | | | | | | | | | | |
| Cu | ++ | | x | x | xx++ | x | xx** | | ++ | xx | ** | ** |
| Ni | xx | xx** | | | | | ** | | | xx | | |
| Cu | ** | | | x | | | ++ | xx | xx | ++ | x++ | xx+ |
| Zn | ** | | xx | xx | | | xx++ | xx | ++ | xx | | xx |
| Fe | | | xx | xx++ | | xx | x | xx** | ++ | xx | x | xx |
| Mn | 2 | | xx | | | xx | | ** | | xx | | xx |
| As | xx** | ++ | | | xx | xx | | | ++ | xx | ++ | ++ |
| Mo | | xx++ | | | | | | | | | ++ | xx |
| Sb | xx | xx | xx | xx | xx | xx | xx++ | | | ++ | ++ | x++ |
| Cd | | xx | | | | | | | | | | |
| Pb | | ++ | | | | ++ | ++ | xx++ | xx | | | |

Abbreviaton: Cr = chromium; Cu = cuprum; Fe = ferrum; Mn = mangan; Ni = nickel; Zn = zink; As = arsen; Mo = Molybdenum; Co = cobalt; Sb = stibium; Cd = cadmium; Pb = plumbum.

Figure 4, spatial map SS010304.050607 shows that Cu and Cr are located far apart and that are in first quadrant and have similarities to As and Fe in third quadrant. Elements of Cu, Pb, Zn and As form strong correlation groups in different quadrants (Figure 4).

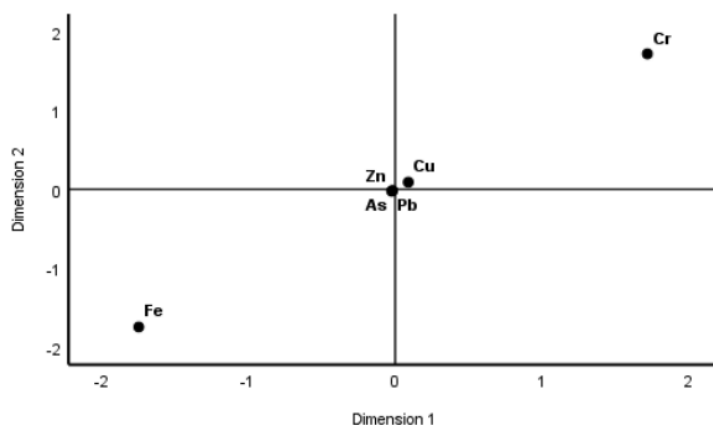


Figure 4. Cu, Zn, Pb, As, Cr and Fe Spatial Map

5. Conclusion

- The Position of Fe and Cr in different quadrant give an indication that the mineralization source are different where Fe is stronger formed as an oxide mineral than Cr forms deposits. Strong estimated that Cr, which forms deposits, is derived from ultramafic rocks so that Cu and Cr are different types of deposits.
- Position of Zn, As and Pb in the spatial image are indications of mineralization in the same rock source compared. Cu, which is close proximity to these three elements, forms different types of deposits even though there are also deposits of Zn, As, and Pb mineralization.

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