

Transaction Report

**GSP-JICA Technical Cooperation Programme
November-December 1999**

Mitsuo Yoshida, JICA Expert in Mineralogy

**Geoscience Laboratory, Geological Survey of Pakistan (GSP)
Japan International Cooperation Agency (JICA)**

December 1999

PREFACE

A short-term technical cooperation programme between Japan International Cooperation Agency (JICA) and Geological Survey of Pakistan (GSP) was held from 22nd November to 27th December 1999, at the premises of Geoscience Laboratory, Geological Survey of Pakistan, Islamabad. JICA dispatched me as a JICA Expert in Mineralogy for conducting the cooperation programme.

Present cooperation has been set as a supplementary programme to the Geoscience Laboratory Project between GSP and JICA, 1991-1997, of which objective is summarized fourfold: (1) maintenance survey, guidance, and fixing of troubled instruments, (2) collaborative works with GeoLab scientists as *on-the-job* trainings in four subjects; *i.e.* environmental mineralogy, environmental magnetism, paleomagnetism, and rare earth elements (REE) exploration in carbonatite body, (3) in-house lecture on some topics in environmental mineralogy and environmental magnetism, (4) other related topics.

This Report contains the summary of present cooperation programme, preliminary research notes that are output from said collaborative works, and lecture notes.

I thank Mohammad Sakhawat, Project Director, and Dr. Allah B. Kausar, Deputy Project Director, Geoscience Laboratory, Geological Survey of Pakistan, for their arrangement and helps in various ways during my stay in GeoLab. I also thank to counterpart scientists in Geoscience Laboratory, Said Rahim Khan, Mohammad Naseem, Ibrar H. Khan, Rehanul Haq Siddiqui, Dr. Tahseenullah Khan, and Dr. Mohammad Ali, for their fruitful cooperation. Special thanks to S. Hasan Gauhar, Director General, Geological Survey of Pakistan; Dr. Masakatsu Sasada, Director, International Cooperation Department, Geological Survey of Japan; Masataka Nakahara, JICA Pakistan Residential Representative; Kazuki Takeuchi, JICA Pakistan Assistant Residential Representative; Mariko Imamura, Regional Department II of JICA Headquarters; and Naoko Yamaguchi, Human Resources Assignment Department of JICA Headquarters.

December 27, 1999
Islamabad

Dr. Mitsuo Yoshida
JICA Expert

SUMMARY

Term: 22nd November 1999 – 27th December 1999

(1) Research Collaboration

Environmental Mineralogy

Objective: Study on heavy metals adsorption property on clay minerals, kaolinite from Salt Range and bentonite from Azad Kashmir

Term: 24th November – 24th December

Counterpart scientists: Mohammad Naseem (Adsorption experiment and AAS analysis), Ibrar H. Khan (EPMA analysis of adsorbents), Rehanul Haq Siddiqui (XRD analysis)

Environmental Magnetism

Objective: Rock magnetic observation on heavy metals contamination of surface soils in and around Islamabad-Rawalpindi urban area, and heavy metal leaching test of the soils.

Term: 04th December – 17th December

Counterpart scientists: Mohammad Ali (Sampling, sample preparation, and magnetic measurements), Mohammad Naseem (Leaching test and AAS analysis)

Paleomagnetism of Oil Reservoir Rocks

Objective: Paleomagnetic study of Jurassic to Tertiary oil reservoir rocks collected from the Meyal #10 well, Potwar basin, with special reference to paleomagnetic dating of hydrocarbon migration timing.

Term: 16th December – 24th December

Counterpart scientists: Mohammad Ali (Analysis)

Cooperator: Pakistan Oil Limited (Sample provider)

REE Exploration

Objective: Field observation of carbonatite body in Koga alkaline igneous complex, Naranji Kandao area, and determination of REE concentration in the carbonatite

Term: 2nd December – 24th December

Counterpart scientists: Said Rahim Khan (Geology, field sampling, sample preparation, interpretation), Mohammad Naseem (ICP analysis), Ibrar H. Khan (EPMA analysis), Mohammad Ali (Field sampling and gamma-ray survey)

(2) Maintenance Survey and Fixing

- EIKO Magnetic Balance (Trouble was fixed, c/p Mohammad Ali)
- Princeton MicroMag 2900 (Trouble by abnormal AC power supply. 3-phase AC voltage regulator shall be installed, c/p Mohammad Ali)
- Natsuhara Spinner Magnetometer (Trouble is caused by a damage of power supply of control NEC-PC98. Trouble was fixed by replacing the NEC-PC98, c/p Mohammad Ali)
- AGICO JR-5A (Trouble was fixed, c/p Mohammad Ali)
- Portable Core Picker (Spare diamond bits will be supplied, c/p Said Rahim)

- Khan)
- ICP (Trouble was caused by impurity of argon gas container. The trouble was fixed based on fax communication with Seiko Instruments Co., c/p Muhammad Naseem)
 - AAS (10 T-shaped glass pipes were supplied, c/p Mohammad Naseem)
 - XRF (Circuit was checked according to manufacturer's inquiry. Repairing shall be done by engineer from the manufacturer)

(3) Lecture

Date: December 23, 1999

Venue: Seminar Room, Geoscience Laboratory

Convener: Ayoub Khalil, Geoscience Laboratory, Geological Survey of Pakistan

Speaker: Mitsuo Yoshida

- 1) Environmental Mineralogy: Applications of Mineral Resources to Environmental Protection and Pollution Control.
- 2) Environmental Magnetism for Anthropogenic Pollution Survey: A Case Study on Contaminated Lake-bottom Sediments.

<Collaboration Topics-I>

Adsorption property of clay minerals, bentonite from Jhelum, Azad Kashmir, and kaolinite from Salt Range: A preliminary results

Objective:

- 1) Technical guidance about adsorption test technique
- 2) Technical guidance about leaching test technique
- 3) Introduction to environmental mineralogy and its applications
- 4) Study on heavy metals adsorption property on clay minerals, kaolinite from Salt Range, bentonite from Azad Kashmir, and zeolite (mordenite) from Sendai, Japan

Counterpart scientists:

Mohammad Naseem (Adsorption experiment and AAS analysis),
Rehanul Haq Siddiqui (XRD analysis),
Ibrar H. Khan (EPMA analysis of adsorbents),

Results:

Two rounds adsorption test were performed for bentonite, kaolinite, and mordenite. These minerals were mineralogically well defined by XRD analysis as well as optical microscopy. The adsorption test was made for 5g powdered clays with 50cc water that contains:

- 1st round test 4ppm of Pb, Zn, Cu, Cr(VI), Cd
2nd round test 2ppm of Pb, Zn, Cu, Cr(VI), Cd, Hg, As, Se

After mixing each clay powder into the solution, different three pH conditions, pH5.0, pH7.0, and pH9.2, were prepared by HCl and Ca(OH)₂. These mixed solutions were shaken 2-hours with an automatic shaker. Then, the mixed solutions were individually separated into residues and water by a centrifugal separator, and the concentration of metal ions in given water was analyzed by an AAS and a mercury detector. The residues were dried and polished thin sections were prepared for EPMA analysis.

Tentative analytical results are shown in Table 1-1 and Figures 1-1, 1-2, and 1-3. Summary of the results is shown in Table 1-2. The bentonite sample from Jhelum, Azad Kashmir shows quite well adsorption property for heavy metals, which is potentially applicable for remediation or environmental protection to heavy metals contaminated sites.

Evaluation:

- (1) Adsorption test techniques were successfully introduced.
- (2) Environmental view points on mineral resources were acquired by c/ps.
- (3) Collaboration between chemist and mineralogist was well functioned.
- (4) Results are probably informative for future environmental application in the country.

Recommendations:

- (1) It is recommended to continue additional adsorption test with other clay minerals in Pakistan, such as other bentonite, Fuller's earth, kaoline clay, halloysite, mica clay, vermiculite, laterite, and so on.
- (2) The results should be published in national or international journal when

above-mentioned additional study was completed.

- (3) It is recommended to enhance the detection limits of heavy metals for environmental purposes. Following values are minimum requirement based on the Environmental Quality Standards, Japan:

Cd	→ 0.01ppm
Pb	→ 0.01ppm
Cr	→ 0.05ppm
As	→ 0.01ppm
Hg	→ 0.0005ppm
Se	→ 0.01ppm
Cu	→ 0.04ppm
Ni	→ 0.01ppm
Mo	→ 0.07ppm
Sb	→0.002ppm
F	→0.8ppm
B	→1.0ppm

- (4) Analysis of anions, especially well-known toxic substances Cr(VI), As, and Se, shall be planned in future.
- (5) EPMA analysis of residual clays shall be attempted.
- (6) Close collaboration between chemist and geologist/mineralogist is required for future success in the subject.

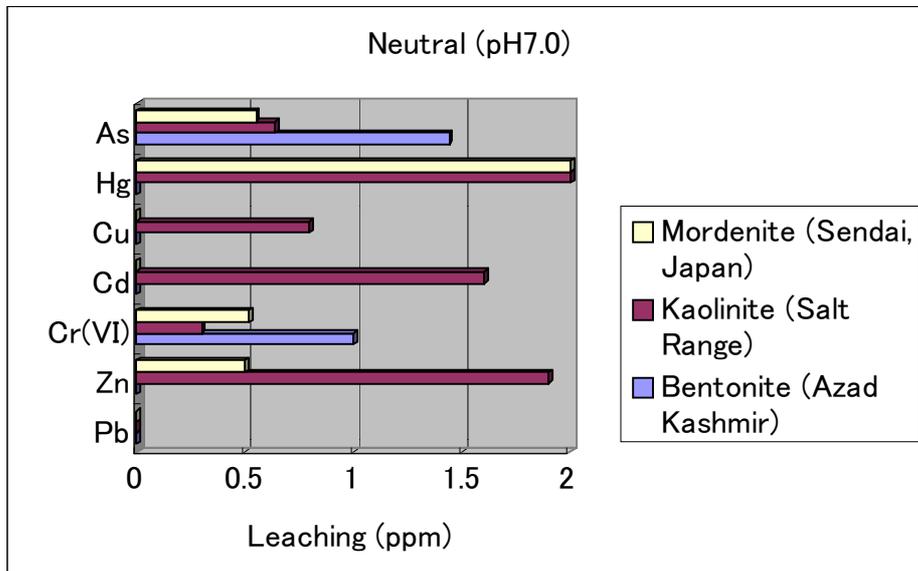


Figure 1-1: Result of 2ppm solution adsorption test (pH7.0)

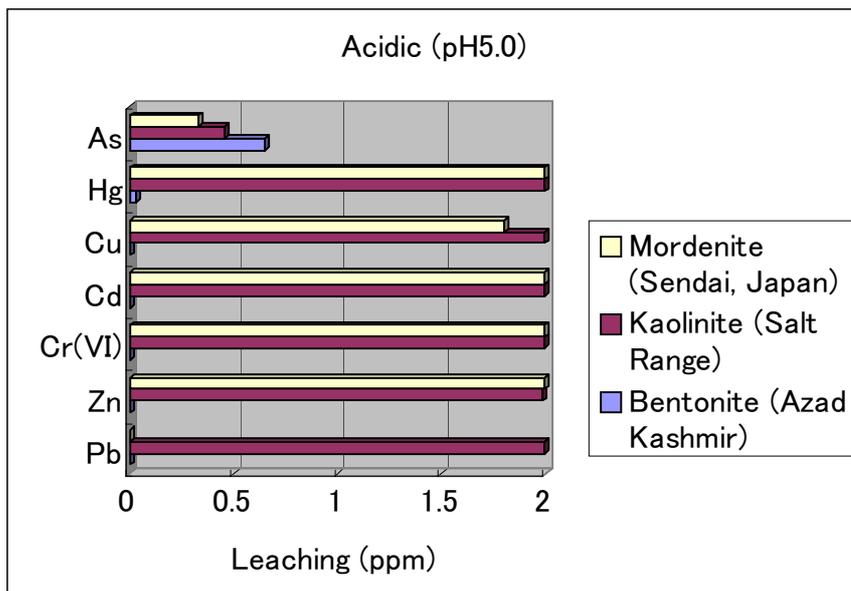


Figure 1-2: Result of 2ppm solution adsorption test (pH5.0)

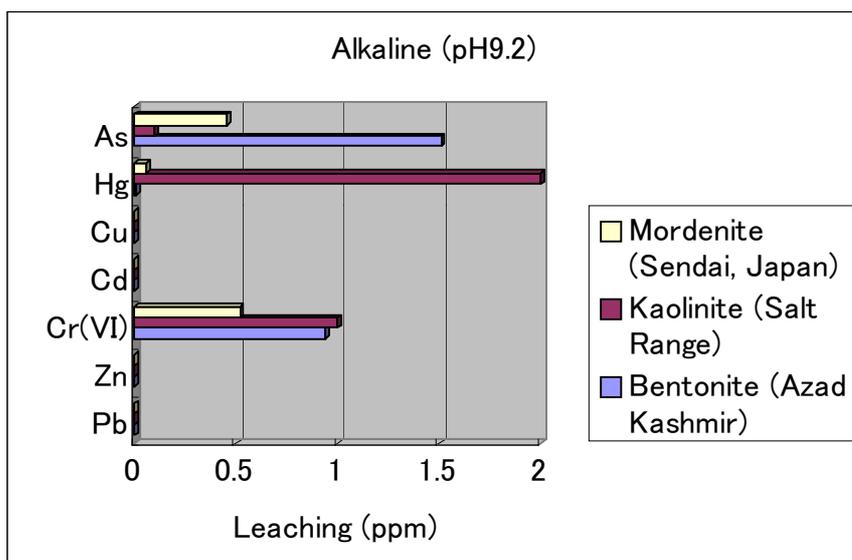


Figure 1-3: Result of 2ppm solution adsorption test (pH9.2)

Table 1-1: Results of Adsorption Test unit: ppm

Acidic (pH5.0) with HCl							
	Pb	Zn	Cr(VI)	Cd	Cu	Hg	As
Bentonite (Azad Kashmir)	nil	nil	nil	nil	nil	0.0287	0.65
Kaolinite (Salt Range)	3	1.99	2	2	2	2	0.46
Mordenite (Sendai, Japan)	nil	2	2	2	1.8	2	0.327
Alkaline (pH9.2) with Ca(OH) ₂							
	Pb	Zn	Cr(VI)	Cd	Cu	Hg	As
Bentonite (Azad Kashmir)	nil	nil	0.94	nil	nil	0.0138	1.51
Kaolinite (Salt Range)	nil	nil	1	nil	nil	2	0.103
Mordenite (Sendai, Japan)	nil	nil	0.52	nil	nil	0.057	0.454
Neutral (pH7.0)							
	Pb	Zn	Cr(VI)	Cd	Cu	Hg	As
Bentonite (Azad Kashmir)	nil	nil	1	nil	nil	0.0026	1.44
Kaolinite (Salt Range)	nil	1.9	0.3	1.6	0.8	2	0.642
Mordenite (Sendai, Japan)	nil	0.5	0.52	nil	nil	2	0.55

1) to each sample added 2ppm of the toxic elements and pH adjusted before shaking 2hr

2) nil means not detected as detection limit (DL) is 0.5ppm for flame mode.

3) DL of Hg and As is 0.01 and 0.02ppm, respectively.

(analyzed by Mohammad Naseem)

Table 1-2: Summary of Adsorption Test

	Bentonite, Jhelum, Azad Kashmir	Kaolinite Salt Range	Mordenite Sendai, Japan
Acidic (pH5.0) Rain water	- Adsorption except As	- Very Poor adsorption	- Poor ion-exchange except Pb
Neutral (pH7.0) Ground water	- Adsorption except Cr(VI), As -Best for Hg	- Poor adsorption except Pb	- Ion-exchange except Zn, Cr(VI), Hg, As
Alkaline (pH9.2) Ca(OH) ₂ treatment	- Adsorption except Cr(VI), As	- Adsorption except Cr(VI), Hg - Best for As	- Ion-exchange except Cr(VI), As
Advantage	- Appropriate for general uses - Best for Hg in neutral condition - Best for Cr(VI) in acidic condition	- Adsorption for As in alkaline	- Stable ion-exchange in alkaline condition

<Topics-II>

Environmental magnetic screening of heavy metals contamination of Islamabad-Rawalpindi urban soils: A preliminary report

Objective:

Rock magnetic observation on heavy metals contamination of surface soils in and around Islamabad-Rawalpindi urban area, and heavy metal leaching test of the soils.

Counterpart scientists:

Mohammad Ali (Sampling, sample preparation, and magnetic measurements)

Mohammad Naseem (Leaching test and AAS analysis)

Results:

A total of 8 samples of surface soil and 3 samples from stream sediments was collected from different locations in Islamabad-Rawalpindi urban area. Five-point Averaging Method was applied for field sampling and sample preparation techniques.

Magnetic susceptibility and leaching property of the samples were analyzed in the paleomagnetic laboratory using Bartington MS-2. The magnetic susceptibility shows clear contrast between soils collected from heavy traffic roadsides and those from green places (Figure 2-1). The background of magnetic susceptibility is around 120×10^{-6} (SI), but two to three times higher in heavy traffic roadsides.

Leaching test was done by chemistry section, where 5g soils from each sample was mingled with 50cc pH7.0 water and leached six hours with an automatic shaker. The leaching was less than the detection limit (0.5ppm) of toxic heavy metals (Table 2-1).

Evaluation:

- (1) Environmental sampling & sample preparation techniques were successfully transferred.
- (2) Techniques of leaching test were successfully introduced.
- (3) Collaboration between chemist and geophysicist was well functioned.
- (4) Results are probably informative for future environmental application in the country.

Recommendations:

- (1) It is recommended to continue additional sampling (screening) and measurement. After the completion of 5km grid sampling, it is better to set some project area for detailed study.
- (2) Not only magnetic susceptibility but also IRM study and magnetic granulometry is probably important for detailed characterization of soils.
- (3) Correlation between magnetic property and leaching is main concern. Thus close collaboration between chemist and magnetic scientist is essential.
- (4) The results should be published in national or international journal when above-mentioned additional study was completed.

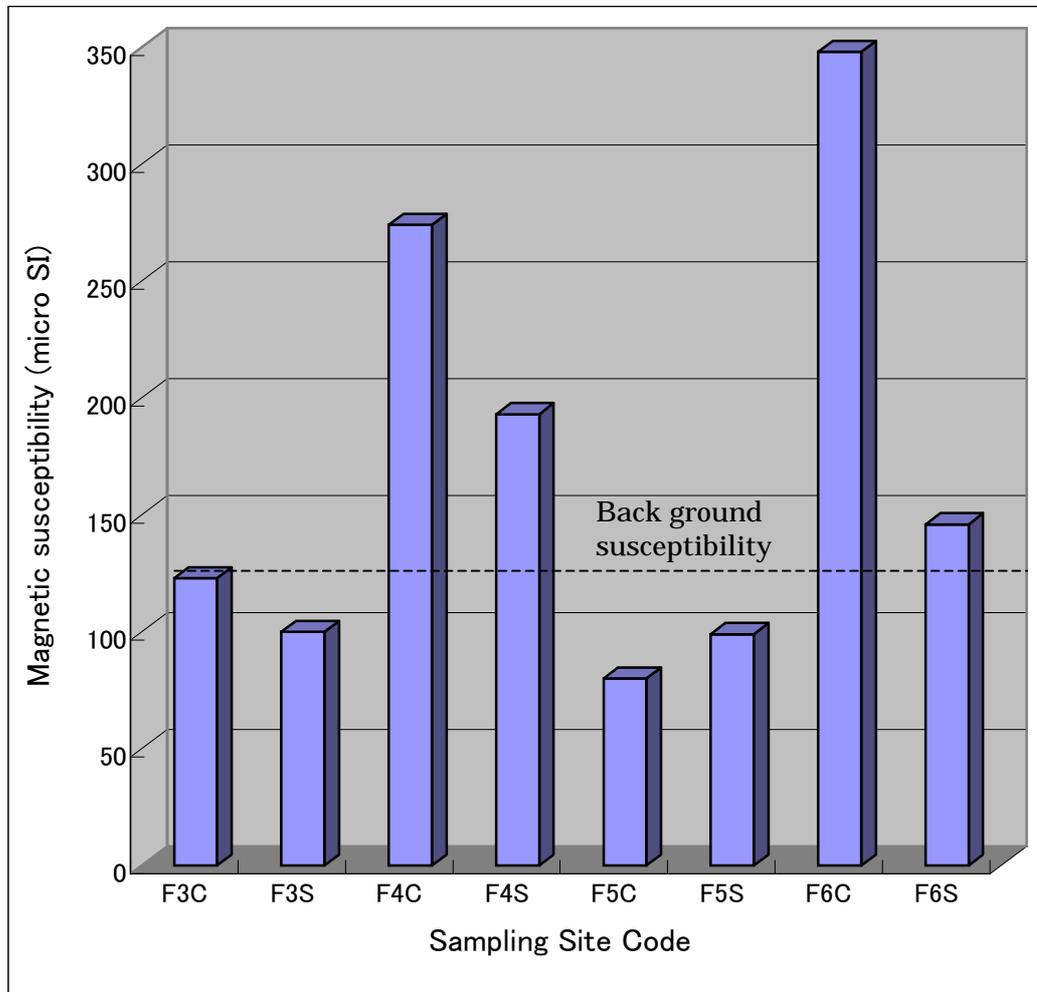


Figure 2-1: Results of magnetic susceptibility measurements of surface soils. F4C, F4S, F6C, and F6S are the heavy traffic road side, while the others are in green zone that probably represent a back ground susceptibility of the area (measured by Mohammad Ali).

Table 2-1: Result of leaching test with pH5.5 water (analyzed by Mohammad Naseem)

	Pb	Zn	Cu	Cr	Cd	Hg	As(ppb)
DN1	NIL	NIL	NIL	NIL	NIL	NIL	19
DN2	NIL	NIL	NIL	NIL	NIL	NIL	30
DN3	NIL	NIL	NIL	NIL	NIL	NIL	26
D4S	NIL	NIL	NIL	NIL	NIL	NIL	15
F5S	NIL	NIL	NIL	NIL	NIL	NIL	27
F6S	NIL	NIL	NIL	NIL	NIL	NIL	16
F3C	NIL	NIL	NIL	NIL	NIL	NIL	29
F4C	NIL	NIL	NIL	NIL	NIL	NIL	26
F5C	Nil	NIL	NIL	NIL	NIL	NIL	24
F6C	NIL	NIL	NIL	NIL	NIL	NIL	14
F3S	NIL	NIL	NIL	NIL	NIL	NIL	26

1) NIL means could not be detected which is 0.5ppm for all the elements except Hg and As.

2) For Hg the detection limit is 10ppb, while for As 20ppb.

(Analyzed by Mohammad Naseem)

<Topics-III>

Rock magnetic Studies of Jurassic oil reservoir rocks in Meyal #10 well, Potwar basin, Pakistan

Objective: Paleomagnetic study of Jurassic to Tertiary oil reservoir rocks collected from the Meyal #10 well, Potwar basin, with special reference to paleomagnetic dating of hydrocarbon migration timing.

Counterpart scientists:

Mohammad Ali (paleomagnetism)

Results:

Tertiary to Jurassic Borehole core samples were provided from the Pakistan Oil Limited for paleomagnetic study.

In order to determine magnetic carrier mineral, a pilot study of core sample collected from oil reservoir sandstone of Jurassic Datta Formation (Box-G) was performed. The pilot study includes lithologic observation of cores, thin section observation, XRD analysis, IRM and hysteresis analysis by MicroMag, thermomagnetic analysis, and NRM measurement with a stepwise demagnetization. The result of analytical observations shows that the magnetization is mostly carried by paramagnetic siderite that is not remanence carrier mineral (Figure 3-1). A trace amount of hematite is also detected but it may be a primary origin. Thus, at least for this pilot sample from Datta sandstone, its paleomagnetic direction acquired at migration time has been hardly maintained. Another problem of given samples is reliability of marked orientation. The orientation of core samples is relied on downward arrows marked by POL engineers, but a case of inconsistent (opposite) orientations was found, which indicate us the orientation is not useful for the vector analysis.

Evaluation:

- (1) What GeoLab could obtain core samples of oil exploration/production well is phenomenal.
- (2) Cooperation between GeoLab and oil company like POL is noteworthy.
- (3) The cores are expected to be very useful for *leading-edge* research on redox magnetization mechanism, which may give a paleomagnetic dating of hydrocarbon migration timing that has been theoretically predicted but practically not yet achieved.

Recommendation:

- (1) The pilot study sounds negative for paleomagnetic research. However it comes from only one sample, which does not represent all cores. Measure magnetic property systematically, and assess its paleomagnetic capacity.
- (2) If paleomagnetic data could not be obtained successfully, but rock magnetic data is very informative for future research.
- (3) The result should be published if POL gives permission.

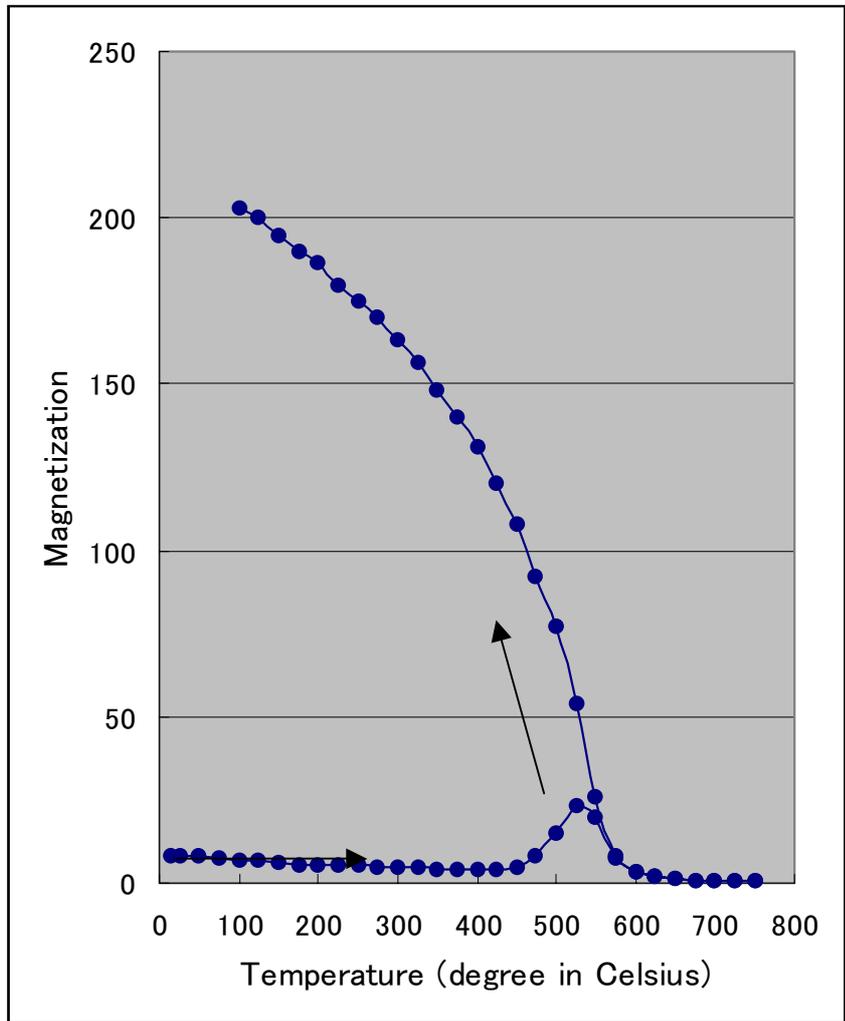


Figure 3-1: Result of thermomagnetic analysis of Datta G oil reservoir rock. The increase in the heating curve around 450-575°C is caused by a decomposition of siderite into magnetite.

<Topics-IV>

Geochemical study of carbonatite body exposed in Naranji Kandao area, Burner District, Swat.

Objective:

Field observation of carbonatite body in Koga alkaline igneous complex, Naranji Kandao area, and determination of REE concentration in the carbonatite

Counterpart scientists:

Said Rahim Khan (Geology, field sampling, sample preparation, interpretation)

Mohammad Naseem (ICP analysis)

Ibrar H. Khan (EPMA analysis)

Mohammad Ali (Field sampling and gamma-ray survey)

Results:

One-day fieldwork was done at 2nd December. The carbonatite exposure was successfully found in the Koga syenite complex, which outcrops more than 1000m² of foothills, immediate north to the Naranji Kandao pass. Ten samples were collected from the carbonatite body, and pulp specimens for chemical analysis and thin sections for optical and EPMA analysis were prepared. Major elements were analyzed by ICP in Geoscience Laboratory, and rare earth elements are analyzing by the ICP as well as ICP-MS in the ACME Laboratory, Canada.

Evaluation:

- (1) Present research is a miscellaneous chapter of previous Koga REE exploration project held by GSP-JICA cooperation project, because at that time typical carbonatite exposure could not be found by the survey team. Present work completed the task and successfully collected carbonatite samples.
- (2) ICP trouble has been fixed, and the performance could be check by present analysis.

Recommendations:

- (1) Detailed field mapping shall be done around the carbonatite body in the Naranji Kandao area.
- (2) Geochemical interpretation is necessary after the completion of analysis.
- (3) Recompile the REE geochemical map published in PGC vol.17.

<Maintenance Problems>

Troubles in Rigaku XRF and Princeton MicroMag instruments

- (1) As already mentioned in previous part, most instruments in GeoLab are properly working at this moment, but two instruments, Rigaku XRF 3370 and Princeton MicroMag 2900 still show troubles.
- (2) The Rigaku XRF 3370 was damaged by abnormal high voltage of AC input. Damaged High Voltage Transformer was replaced, but still the XRF is not properly working. Based on the results of some checking with Dr. Tahseenullah Khan and fax communications with RIGAKU and Dr. Shirahase, it has been concluded that the trouble was caused by not only a damage of the high voltage transformer but also that of the X-ray output controller.
- (3) Princeton MicroMag is also a victim of abnormal high voltage AC input (three-phase source). Fortunately, the instrument was protected by self-guard system to high voltage, and no severe damage was occurred inside. However it can not be operated under a high voltage (>240V 3-phase). Thus, a 3-phase voltage regulator is recommended to deploy between the MicroMag power and 3-phase AC source. The regulator will be supplied by JICA Pakistan office. Before the deploy, instrument users should check the voltage of 3-phase AC, and if the voltage is above 240V, do not use the instrument for avoiding further troubles.
- (4) Almost all the troubles with instruments are caused by poorly regulated AC source supplied by the WAPDA line. It is strongly recommended to check the AC source.