International Committee for Coal and Organic Petrology
Commission I

Handbook of Instrumental Techniques Applied in Coal and Organic Petrology

Electron Microprobe

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65th ICCP Meeting, 25 – 30 August 2013 Sosnowiec, Poland

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International Committee for Coal and Organic Petrology
Handbook of Instrumental Techniques
Applied in Coal and Organic Petrology
Electron Microprobe

Part I:

The Instrument (Capabilities, limitations, development of analytical protocols, standards etc.

Part II:

Coal macerals and source rocks studies using EMA

References

Recommendations to ICCP

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Applied in Coal and Organic Petrology
Electron Microprobe

Naturally occurring organic matter comprises distinct and complex mixtures of components (macerals) of

- various origins,
- distinct chemistries and, consequently,
- different utility with respect to hydrocarbon generation and technological applications

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Significance

The electron microprobe gives a unique opportunity to investigate simultaneously both the in-situ chemistry of coal macerals (C, O, N, S), and the major, minor, and trace elements matter present in the same coal sample.

- Mineral characterisation (e.g. clay compositions),
- Fluorescing clay minerals
- Mapping minor and trace element occurrence (e.g. arsenic, phosphorus)

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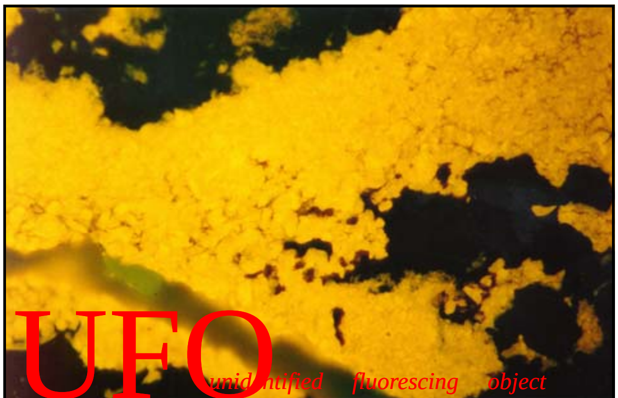

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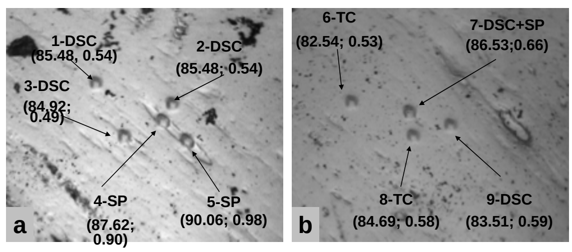
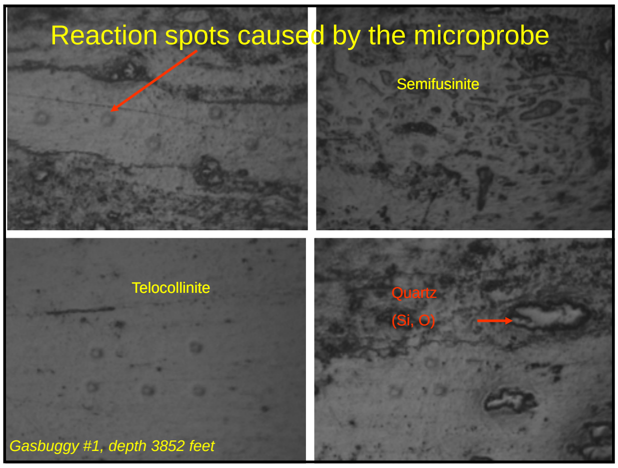


Electron Microprobe



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Electron Microprobe

- The conjunction of organic petrography with other analytical techniques is of capital importance
  - in making advances in the knowledge of organic matter and in addressing key questions and
  - assessing evolving trends regarding the use of coal and other solid fuels

(*Suárez-Ruiz et al, 2012).*

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- A t review by Suárez-Ruiz et al. (2012) noted that the chemistry of coal macerals has been the object of multiple investigations, particularly in the last 25 years due to both the development of maceral separation techniques (e.g., Dyrkacz and Horwitz, 1982; Dyrkacz et al., 1984; Honaker et al., 1996) and the refining and development of analytical tools to probe the chemistry of macerals in situ and its behaviour upon heating.
- Some examples of these types of maceral studies are listed (References) but no attempt has been made to evaluate the contribution of the electron microprobe to advance science of coal petrology.

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Capabilities

- Understanding the nature of some of the coal macerals and kerogen in source rocks is not always possible because a mechanical separation of macerals is a tedious process and separation is not always satisfactory, especially for such components as:
  - Alginite, amorphous organic matter
  - Bitumen, pyrobitumen,
  - Secretinite,
  - Pseudovitrinite

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Capabilities

Microprobe analysis can indicate:

- ❑Coalification tracks of macerals with rank advance and in defining coalification jumps
- ❑Inorganic elements that may react unfavourably in combustion or gasification or may survive demineralisation processes
- ❑Detailed nature of cleat and other mineralisation that may affect gas drainage or CO_2 storage

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Distribution of Sulphur & Nitrogen

- Can led to a better understanding of sulphur incorporation into sedimentary organic matter.
- Such findings may in turn be used to develop an effective desulfurization process that would target those organic compounds or structures that are specifically high in S
  - *as suggested for example by Demir and Harvey (1991).*

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Capabilities

Interactions between macerals (e.g. sporinite-vitrinite, inertinite-vitrinite)

(Mastalerz et al., 1993a,b)

Tracking maceral changes during utilization and Char and coke characterization

(e.g. Walker and Mastalerz, 2004)

Coal oxidation studies (e.g. Pseudovitrinite characterization)

(Gurba 1998, Gurba and Ward, 2000)

Reconciling petrographic data with ultimate analysis

(Bustin et al., 1993, 1996, Ward et al., 2008).

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Mapping Inorganic Elements

Ca, P, S, Si, Al and Fe

- Elemental microprobe X-ray mapping of the elements Ca, P, S, Si, Al and Fe can provide an initial fingerprint of the elemental distribution and can be a useful tool for understanding the relationship between minerals and macerals within coals
- Inorganic elements may react unfavourably in combustion or gasification or may survive demineralisation processes

(Gurba et al., 2003, Li et al., 2007, 2010).

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Micro-cleat mineralisation

EMPA can provide knowledge of the organic matter chemistry along with detailed nature of cleat and other mineralisation

- that may affect shale gas and coal seam gas drainage and
- also be useful in evaluating coal seams for CO_2 geological storage.

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Petroleum Source Rocks

The study by Mónaco et al. (2007) shows that the use of EPMA for the determination of the purity of isolated kerogens, studied together with the chemical analysis of major and trace elements,

- allows obtaining information about the **associations of elements with the mineral phases or the kerogen** in petroleum source rocks.

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Astrobiological

High resolution mapping of carbon and other co-distributed elements can provide an important first step in the astrobiological interrogation of extraplanetary materials

(Boyce et al., 2001)

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Petroleum Source Rocks

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- Over the last two decades the International Committee for Coal and Organic Petrology (ICCP) has refined the description of macerals and revised their nomenclature:
  - ICCP, (1998, 2001) for vitrinite and inertinite maceral groups respectively, and
  - Sýkorová et al., 2005 for huminite macerals).
- The ICCP also currently is preparing an updated description and classification of organic components included in the liptinite group (Suárez-Ruiz et al, 2012).

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Electron Microprobe

- ICCP 1994 System – *Vitrinite and Inertinite Classification* – description of maceral groups lacks of chemical properties
- According to ICCP (1998): No information is available on the chemical composition of pure collotelinite….

Recommendations

Provide update to ICCP classification of Vitrinite (ICCP, 1998) and Inertinite (ICCP, 2001) on elemental composition of macerals.

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- All data on elemental composition of macerals [C, O, N & S] along with VR have been tabulated with age, location, references, etc

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EMPA provides knowledge of the in-situ elemental chemistry of the organic matter (C, O, N, S) in coal and kerogens.

Significance

EMPA provides an improved basis for evaluating coal and dispersed organic matter (including source rocks and possibly hydrocarbon residues)

- in petroleum exploration, or for evaluating transformations of coal macerals in different utilisation processes.

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Electron Microprobe Working Group Objectives:

- Make new analytical methods increasingly more applicable in studying in-situ organic matter
- Standardize procedures
- Provide information and advice on:
  - standards
  - reproducibility
- and to extend their applicability to a larger number of research centres;

Round Robin Exercise

Element Analysed	Anthracite Standard			High-Volatile Bituminous (Australia)			
	ASTM	UNSW	IU	UNSW		IU	
	(%, daf)	(%, wt)	(%, wt)	(%, wt)	SD	(%, wt)	SD
Carbon (C)	93.84	93.13	93.30	85.23		85.62	0.72
Oxygen (O)	2.81	2.38	1.48	7.89		7.33	0.44
Nitrogen (N)	1.03	1.04	0.85	1.73		1.46	0.47
Sulphur (S)	0.55	0.39	0.41	0.60		0.72	0.05
Iron (Fe)	-	0.07	0.06				
Calcium (Ca)	-	0.01	0.02				
Chlorine (Cl)	0.01	-	0.01				
Silicone (Si)	-	-	-				
Aluminum (Al)	-	-	-				
Hydrogen (H)	1.76	*	*	*	*	*	*

2000-2001 Other Activities

Determination of Nitrogen Using an Electron Microprobe –Experimental Procedure

During September – October 2000 analytical procedure was tested for nitrogen determination using CAMECA SX 50 microprobe analyser. The results are published in International Journal of Coal Geology (Mastalerz and Gurba, 2001).

Proposed Activity for 2001/2002

- Further testing standards for carbon determination;
- Testing standards for oxygen determination;

Some examples of how the electron microprobe may be used in maturation studies include:

(1) use of carbon and oxygen content of telocollinite as a rank parameter in regional maturation studies;

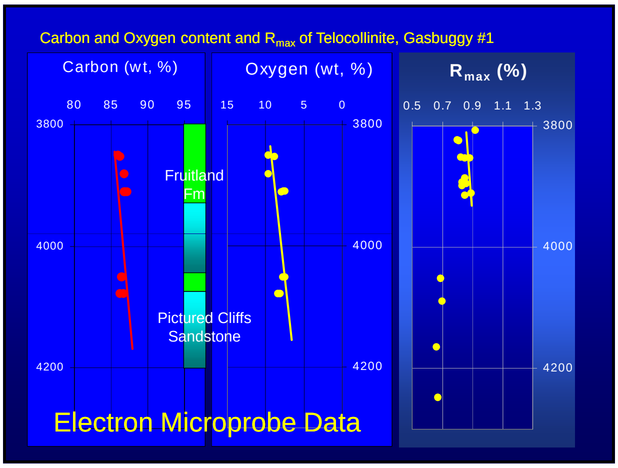
(2) evaluation of the relationship between vitrinite reflectance and the elemental composition of macerals in marine-influenced coals (chemistry of vitrinite reflectance suppression);

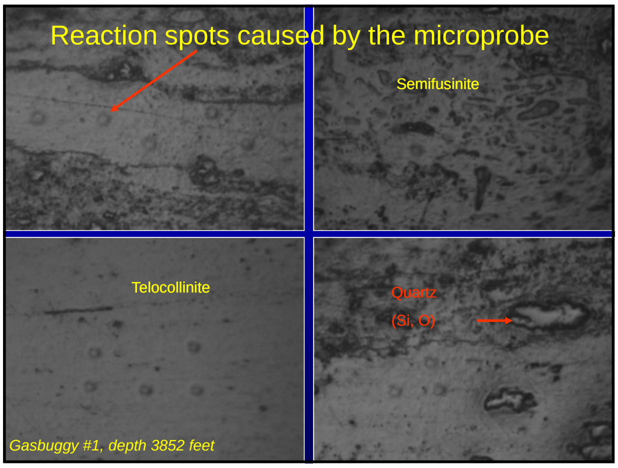
APPLICATION OF ELECTRON MICROPROBE TECHNIQUES IN COAL RANK STUDIES

Lila W. Gurba

"Every coal researcher must be warned for this fact; only by direct oxygen determination is one able to check whether the element balance is right or not"
Van Krevelen, 1993.

School of Geology, The University of New South Wales, Sydney





Cameca SX-50 Electron Microprobe
The University of New South Wales

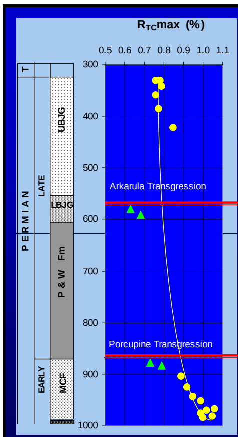
- Four wavelength-dispersive spectrometers
- TAP, PET, PC0, PC1 and PC2 analyzing crystals
- accelerating voltage of 15 kV
- beam current of 10nA
- beam diameter of 2-5 µm

Element	Standard
Carbon	*Anthracite*
Oxygen	*Sanidine*
Nitrogen	*Boron nitride*
Sulphur	*Barite*
Iron	*Hematite*
Silicon	*Quartz*
Aluminum	*Sanidine*
Calcium	*Dolomite*

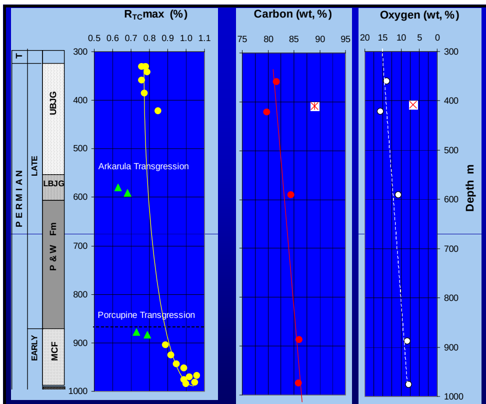
MATURATION STUDIES

- Carbon and oxygen of telocollinite as a rank parameter in regional rank studies;
- Vitrinite reflectance anomalies
  - Relationship between vitrinite reflectance and its chemistry in marine-influenced coals;
  - Carbon/oxygen relationship in heat-affected coals due to igneous intrusions.

Mean Maximum Vitrinite (Telocollinite) Reflectance



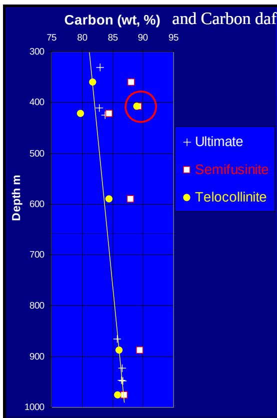
Gunnedah Basin, Australia



C and O follow Hilt's law

Gunnedah Basin, Australia

Electron microprobe data averaged for telocollinite in each individual sample



Electron microprobe carbon content of telocollinite and semifusinite against depth

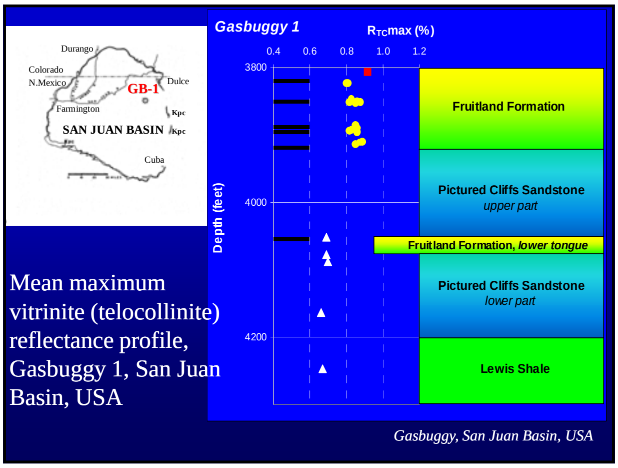
- coalification track of macerals
- telocollinite and semifusinite join at 89-90%

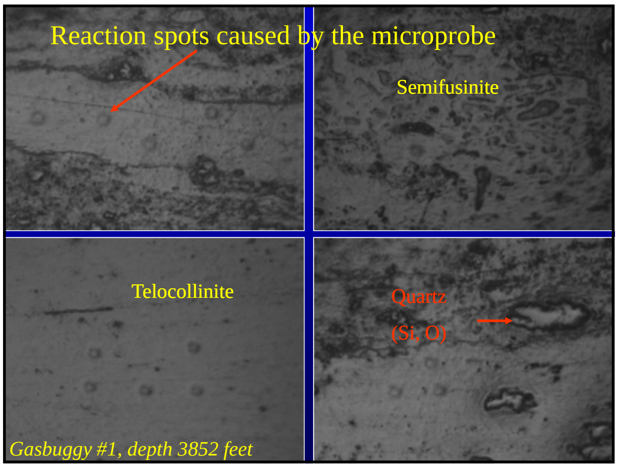
Whole-coal ultimate carbon

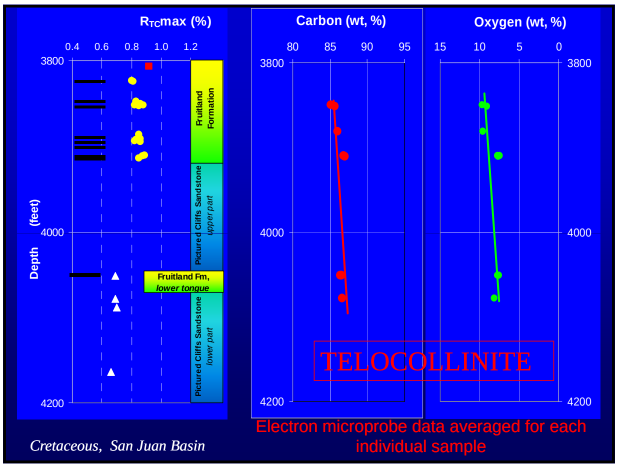
- chemical composition is controlled by coal type and rank

Bando, Gunnedah Basin, Australia

Electron Microprobe Handbook EG, 65th ICCP, August 2013, Sosnowiec, Poland







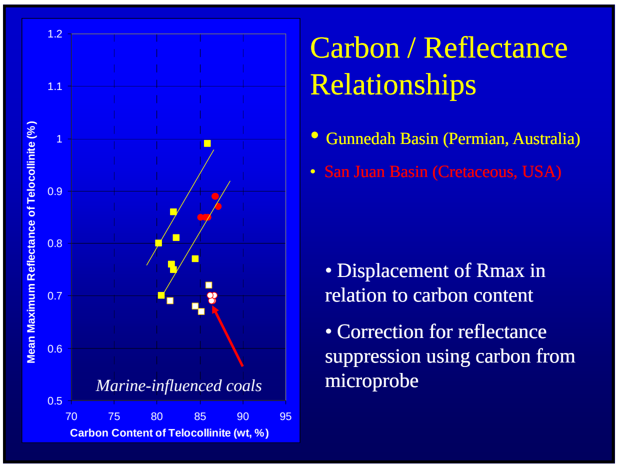
Electron Microprobe Data on Telocollinite

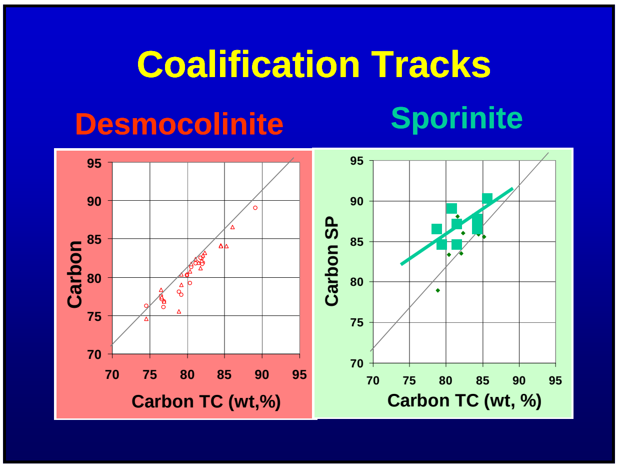
	C	O	N	S	R_{max}
Depth (ft)	wt %	wt %	wt %	wt %	%
3850	85.1	9.7	1.7	0.7	0.82
3852	85.7	9.0	1.4	0.7	0.85
3881	86.0	8.8	1.6	0.6	0.85
3910	86.8	7.5	1.6	1.0	0.89
3910	86.9	7.7	1.8	0.9	0.89
3911	87.1	7.9	1.5	0.8	0.85
4051	86.5	7.8	1.8	0.8	0.69
4078	86.7		1.4	0.7	0.70

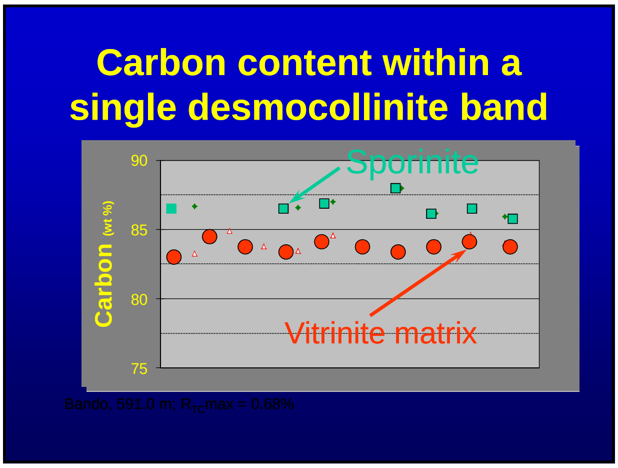
Gasbuggy 1, San Juan Basin, USA

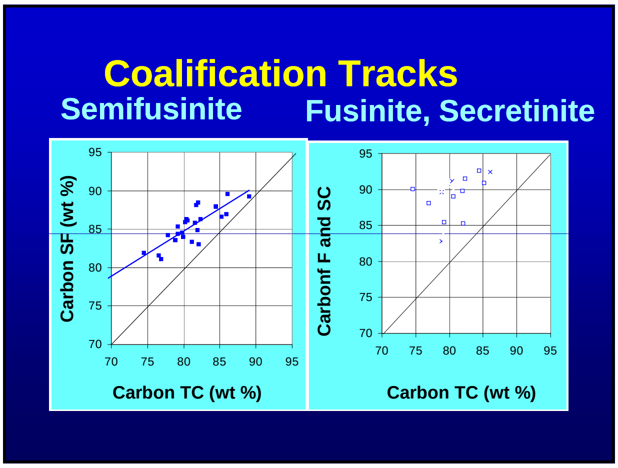
Marine-influenced Coals

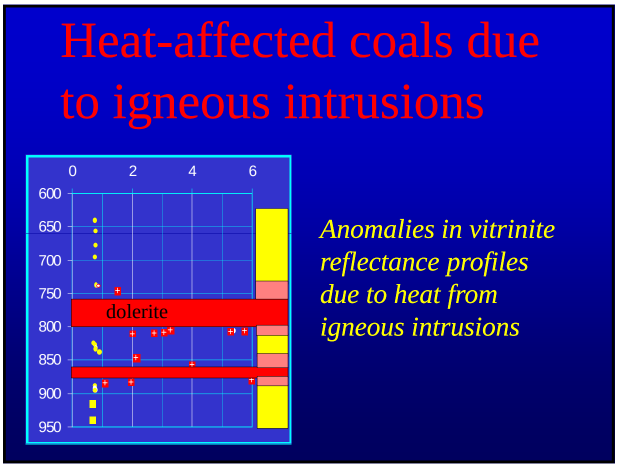
(Reflectance Suppression)

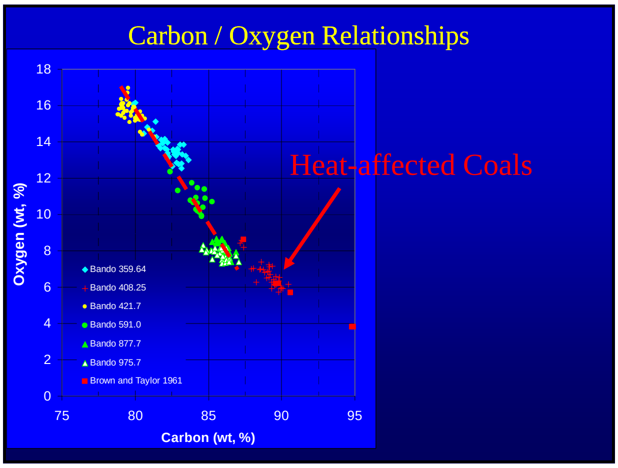


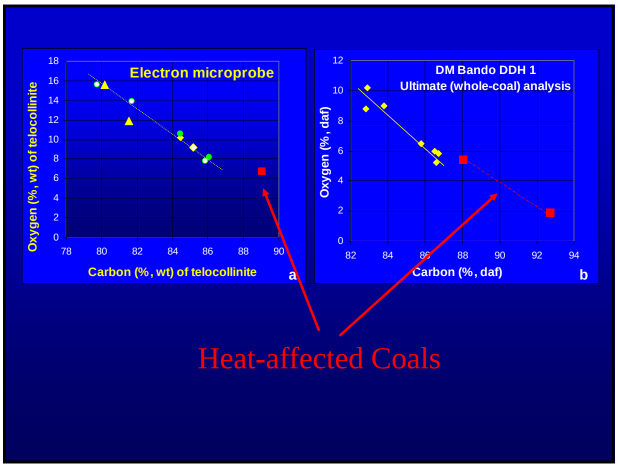

Coalification Tracks
Desmocolinite
Sporinite
Carbon
Carbon TC (wt,%)
Carbon SP
Carbon TC (wt, %)


Carbon content within a single desmocollinite band
Sporinite
Vitrinite matrix
Carbon (wt %)


Coalification Tracks
Semifusinite
Fusinite, Secretinite
Carbon SF (wt %)
Carbon TC (wt %)
Carbonf F and SC
Carbon TC (wt %)


Heat-affected coals due to igneous intrusions
dolerite
Anomalies in vitrinite reflectance profiles due to heat from igneous intrusions


Carbon / Oxygen Relationships
Heat-affected Coals
Oxygen (wt, %)
Carbon (wt, %)
Bando 359.64
Bando 408.25
Bando 421.7
Bando 591.0
Bando 877.7
Bando 975.7
Brown and Taylor 1961


Electron microprobe
Oxygen (%, wt) of telocollinite
Carbon (%, wt) of telocollinite
a
DM Bando DDH 1
Ultimate (whole-coal) analysis
Oxygen (%, daf)
Carbon (%, daf)
b
Heat-affected Coals

Conclusions
Electron Microprobe and Maturation Studies

Heat-affected coals

Coals affected by igneous intrusion show a different relationship between carbon and oxygen of vitrinite (telocollinite), relative to coals where the rank is determined by depth of burial alone

Conclusions
Electron Microprobe and Maturation Studies

Marine - influenced coals

- Vitrinite (telocollinite) in marine influenced coals has anomalously low reflectance, but shows no more than a small variation in carbon content.
- No enrichment in organic sulphur in marine-influenced vitrinite in relation to iso-rank non-marine influenced vitrinite in the same vertical sequence has been noted.

Conclusions
Electron Microprobe and Maturation Studies

The Mystery of Vitrinite Reflectance Suppression

Marine-influenced coals show a different relationship between maximum vitrinite (telocollinite) reflectance and carbon content relative to coals not subject to marine influence.

Conclusions
Electron Microprobe and Maturation Studies

The Mystery of Vitrinite Reflectance Suppression

- The magnitude of reflectance suppression may be estimated based on carbon content determined by electron microprobe and the vitrinite reflectance/carbon relationship for normal coals.

Conclusions
Electron Microprobe and Maturation Studies

Carbon content of vitrinite (telocollinite) determined by electron microprobe -

useful alternative to vitrinite reflectance as a rank indicator in maturation studies.

Non-mineral Inorganics in Low-rank Coals

The inorganic elements in low-rank coals often occur as direct components of the organic compounds (e.g. as ions attached to carboxylate groups).

Unlike minerals, they do not necessarily occur as oxides.

The corrections for O, C and S do not apply to such inorganic components.

Applications of Electron Microprobe Data

- Reconciling petrographic data with ultimate analysis
- Partitioning of S and other elements among macerals
- Mineral characterisation (e.g. clay compositions)
- Mapping trace element occurrence (e.g. arsenic)

Applications of Electron Microprobe Data

- Interactions between macerals (e.g. sporinite-vitrinite)
- Rank and maturation studies
  - more robust rank indicator than vitrinite reflectance
- Coal oxidation studies
- Tracking maceral changes during utilisation
- Char and coke characterisation