A GEOCHEMICAL AND MINERALOGICAL COMPARISON OF OLIGOCENE LIGNITES FROM THE BOVEY BASIN, DEVON AND THE CRUMLIN SUB-BASIN, NORTHERN IRELAND

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The compositions of lignites from the Bovey Basin, Devon and the Crumlin sub-basin in the Lough Neagh area of Northern Ireland are characteristically different and reflect local geology (Hercynian granite and Tertiary basalt respectively). The inorganic mineral assemblage in Bovey Basin lignite consists of kaolinite, illite and quartz, whereas lignite from the Crumlin sub-basin contains kaolinite, quartz and calcite.

Bovey Basin lignite contains higher concentrations of Cu, Rb, Y and Sr, with Lough Neagh Group lignite containing higher TiO_2, Cr, Mn, Ni, V and Zr. The range of 'immobile element' ratios (Y, Ti, Zr, Nb) in Bovey Basin lignite is similar to that of Dartmoor Granite samples, and dissimilar to that of the locally extensive Crackington Formation. It is suggested that the weathering products of Tertiary basalts dominate the inorganic fraction of the Crumlin lignites.

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INTRODUCTION

This paper compares the inorganic geochemistry of lignite from the Bovey Basin, Devon, with Lough Neagh Group lignite from the Crumlin sub-basin, Northern Ireland. The inorganic composition of lignite is largely controlled by the composition of the fine-grained inorganic detrital sediment which it contains, and the composition of this argillaceous material generally reflects the composition of its source region (McCaffrey 1992 and references therein). By comparing the more 'immobile' element ratios of possible source areas with those of the lignite, it will be suggested that the provenance of the inorganic fraction of the lignite may be inferred.

BOVEY BASIN AND LOUGH NEAGH GROUP BASINS: A COMPARISON

The Bovey Basin and the small adjacent Decoy Basin to the south were formed by subsidence controlled by the Lustleigh-Sticklepath Fault System (Fasham, 1971; Edwards, 1976; Wilkinson *et al.,* 1980; Selwood *et al.,* 1984) (Figure 1). Using gravity modelling, Fasham, (1971) has suggested that a maximum of 1245 m of sediments is preserved in the Bovey Basin although only the top 300 m of the basin have been drilled. The sediments consist of kaolinitic clays, sandy and silty clays, silts, lignites and sands. Palynological analysis suggests that the topmost 300 m of sediments of the Bovey Basin are early to middle Oligocene in age,

with Eocene age sediments having been suggested to occur lower down in the succession (Edwards, 1976; Wilkinson *et al.,* 1980). Sedimentation took place on river flood plains and to a lesser extent in lakes (Selwood *et al.,* 1984).

The late Oligocene (Chattian) Lough Neagh Group (LNG) is composed of fluvial, deltaic and lacustrine sandstones, mudstones and lignites and was deposited in a series of partially fault-bounded sag basins on the Palaeocene basalts of the Antrim Lava Group (Wilkinson *et al.,* 1980; Griffith *et al.,* 1987; Parnell *et al.,* 1989; Parnell and Meighan, 1989) (Figure 1). At least three small basins containing LNG sediments occur to the north-west of the Tow Valley Fault in northern Antrim, although the most extensive occurrence of LNG sediments is in and around the vicinity of the present-day Lough Neagh. The 9 km^2 Crumlin sub-basin occurs onshore to the east of Lough Neagh and contains conglomerate, mudstone, sand and extensive lignites. Meighan *et al.* (1989), Shukla (1989) and McCaffrey (1992) have argued that the weathering products of the Tertiary basalts dominate the inorganic fraction of the Lough Neagh Group lignites.

The clay mineral assemblages sampled in lignites from the Bovey Basin and Crumlin sub-basin have not been deeply buried and are unlikely to have undergone significant burial alteration (Shaw, 1981). However, early diagenetic effects (silicification, growth of siderite) have been observed in the Lough Neagh Group (Shukla 1989).
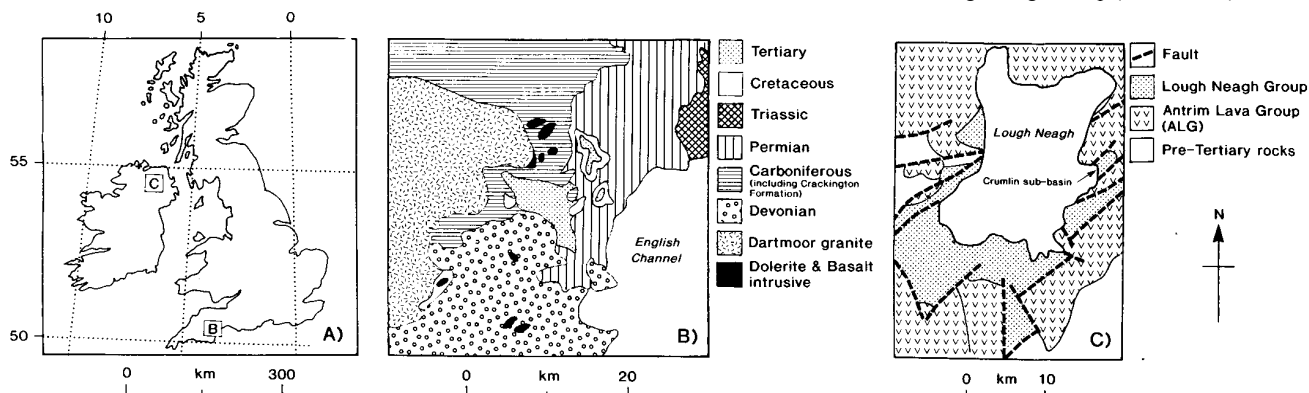

Figure 1: Locality and outline geology maps for the Bovey Basin and the Crumlin sub-basin.

CONTROVERSY OF BOVEY BASIN SEDIMENT PROVENANCE

Early authors (references in Selwood et al., 1984) considered that the infill of the Bovey Basin was derived from decomposed Dartmoor Granite. Selwood *et al.* (1984) suggested that weathering products of 'sedimentary rocks' and the nearby Dartmoor Granite were likely sources for the detritus of the Bovey Basin. Lateritic profiles in local residual gravels have been used to infer tropical weathering conditions during the deposition of Tertiary sediments in the Bovey Basin (Isaacs, 1976; Sellwood and Sladen, 1981). Tropical weathering of Devonian and Carboniferous sedimentary rocks (which include the locally extensive Crackington Formation; Figure 1) has been suggested as the origin of the pure kaolinite beds in the basin (Edwards, 1976; Sellwood and Sladen, 1981).

LIGNITE GEOCHEMISTRY

The variation in mineralogy and bulk geochemistry of lignite and coal may be used to provide insights into swamp formation processes, palaeogeography and provenance (McCaffrey, 1992). Lignite mineralogy and bulk geochemistry are also of commercial relevance, since the concentration of various elements may influence lignite utilisation. Lignite composition affects boiler slagging and corrosion, catalysis poisoning and emission of pollutants (Dewison and Kanaris-Sotiriou, 1986; Couch, 1988).

In addition to elements contained within inorganic minerals present in lignite, other elements such as Ca, Fe, K, Mg, Mn and Na may be partly organically associated (McCaffrey, 1992). In this study, the ash content of samples of lignite from the Crumlin sub-basin was measured by ashing at 700°C for 1 hour. The ash content of samples of lignite from the Bovey Basin was measured by weighing the dried residue of lignite oxidised by hydrogen peroxide for 100 hours at 60°C. Both ashing methods eliminate organic matter, although the relative efficiency of the two techniques is not known. Ash to element correlation coefficients calculated using different ashing procedures are not directly comparable. However, correlation coefficients for Bovey Basin and Crumlin sub-basin lignite samples indicate the relative degree of association of elements with ash content for each set of data. In this paper elements that are strongly associated with inorganic matter are presumed to be accommodated within (detrital) mineral matter.

SAMPLING

69 samples from a lignite seam exposed in the Newbridge Quarry, in the Bovey Basin, Devon, were obtained over a distance of 200 m with sample points 3 m apart (samples BT 1 to BT 69) (McCaffrey, 1992). Small (c. 25 g) samples were taken from the lignite seam at a height of 20 cm above a prominent dirt band. 75 samples analysed from the Crumlin sub-basin are sub-samples of borehole core from the top, middle and base of the Aghnadarragh Lignite Member (McCaffrey, 1992). The boreholes are spread evenly throughout the area of the sub-basin although their exact positions are confidential.

ANALYTICAL METHODS

XRD

Qualitative XRD experiments with finely powdered whole lignites from the Bovey Basin show that clays are present in all samples studied and that other crystalline phases are generally of minor importance. H_2O_2 oxidation of lignite organic matter was used to enable recovery of clay minerals from whole lignite samples. Apart from clay minerals, only quartz peaks and minor calcite were observed on diffractograms from oxidised residues of lignites from the Bovey Basin and the Crumlin sub-basin, and complete recovery of all mineral phases is assumed to have been achieved.

Samples were prepared for XRD analysis by gently powdering residues from oxidation using a pestle and mortar. 0.5 g of powder was mixed with approximately 0.3 cm³ distilled water, pipetted onto a glass slide and allowed to dry.

Analysis of specimens took place on a Siemens D5000 diffractometer using a Cu anode X-ray tube at 40kV, 30 mA and a diffracted-beam graphite monochromator. A step size of 0.04° and a count time of 4 secs step[-1] were found to give optimum results in terms of time per scan and peak resolution. Samples of Bovey Basin lignites were scanned from 2° 2θ to allow analysis of any mixed layer clays. Since no mixed layer clays were observed, a faster scanning program was used for the majority of Crumlin samples, starting at 5° 2θ. All diffractograms had background subtracted and were scaled to give 750 counts for a full-scale peak, using Siemens 'Diffrac-At' software. The mineral phases were identified by peak matching using Siemens search/match software and the JCPDS powder diffraction database, as well as sample glycolation and heating (see below).

Laboratory-grade glycerol was used to glycolate specimens which were then allowed to dry for at least 72 hours. Heating of the glycolated specimens for 1 hour at 450°C and at 550°C took place in an electric muffle furnace. Glycolation did not cause shifts in any peaks and the possible presence of expandable clays was therefore discounted. The presence of weddellite (see below) and kaolinite was confirmed through peak breakdown after heating samples to 450°C and 550°C respectively.

XRF

Samples of lignite were air dried for 24 hours, prior to further drying at 105°C overnight. The lignite samples were powdered for 10 seconds each using a Tema laboratory disc mill with a WC barrel. The lignite powder was re-dried in bottles at 105°C overnight.

14 g of dried lignite powder were then mixed with about 20 drops of PVA binder and compacted in a pellet-dye by a bench press at a pressure of 25 tonnes inch[-2] for 3 minutes. The pellets were then allowed to dry slowly in a warm oven. A suite of elements (Ti, Fe, Ba, Cr, Cu, Mn, Ni, Rb, Sc, Sr, V, Y, Zn, Zr) were analysed on the whole lignite powder pellets using a Siemens SRS 303AS automatic X-ray spectrometer with a Rh X-ray tube.
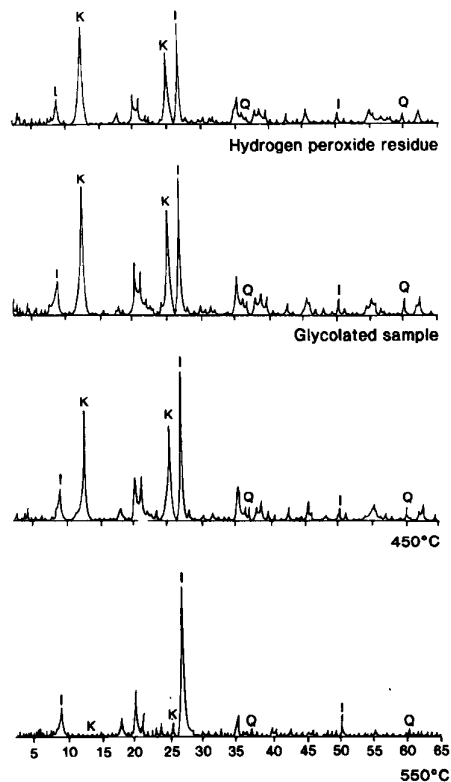

Figure 2: Diffractograms of Bovey Basin lignite showing the effects of glycolation and heating to 450oC and to 550oC. The main peaks of the identified phases are labelled (1=illite, K=kaolinite, Q=quartz).
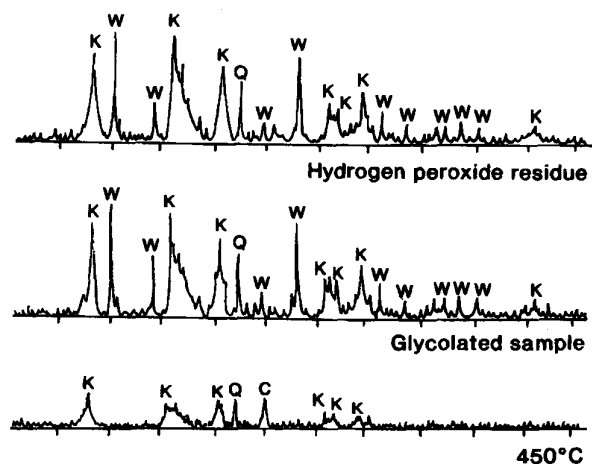
Figure 3: Diffractograms of Crumlin sub-basin lignite showing the effects of glycolation and heating to 450°C and to 550°C. The main peaks of the identified phases are labelled (K=kaolinite, W=weddellite, Q=quartz, C=calcite).

RESULTS

Mineralogy

Bovey Basin:

The main minerals identified in samples from the Bovey Basin were kaolinite, illite and quartz (Figure 2.). The distinct kaolinite peaks seen at 12° 2θ and 24.5° 2θ on hydrogen peroxide residue diffractograms were unaltered by glycolation and were still present after heating the samples to 450°C, but were absent after the samples had been heated to 550°C, at which point kaolinite had largely broken down. The distinct illite peaks at 8.5° 2θ, 26.7° 2θ and 50.1° 2θ were unaltered by glycolation or heating to 550°C. Quartz peaks mainly coincided with illite peaks, but were observed at 36.6° 2θ and 60° 2θ.

The kaolinite present in Bovey Basin lignite is likely to have been derived through tropical weathering of local rocks under acid conditions (Shaw, 1981; Deer *et al.*, 1966). Detrital illite is generally considered to be generated initially through weathering of feldspars and other aluminosilicates in temperate, alkaline environments. Such conditions may have occurred during deposition of local Devonian and Carboniferous sediments, and illite may subsequently have been derived from weathering of these sedimentary rocks (House, 1981). Authigenic illite growth through the breakdown of kaolinite is unlikely to have occurred in the humic acid-rich lignite, although the reverse reaction has been suggested in Ontario lignite (Van Der Flier-Keller and Fyfe, 1988). The clay-dominated mineral suite of Bovey Basin lignite represents deposition in low energy waters and samples which contain no mineral matter may be entirely woody material.

Crumlin sub-basin:

The main minerals identified in samples from the Crumlin sub-basin were kaolinite, weddellite and quartz, with minor calcite in some diffractograms (Figure 3). Weddellite is a calcium oxalate hydrate and is an experimental artefact, crystallising after the lignite has been treated with hydrogen peroxide.
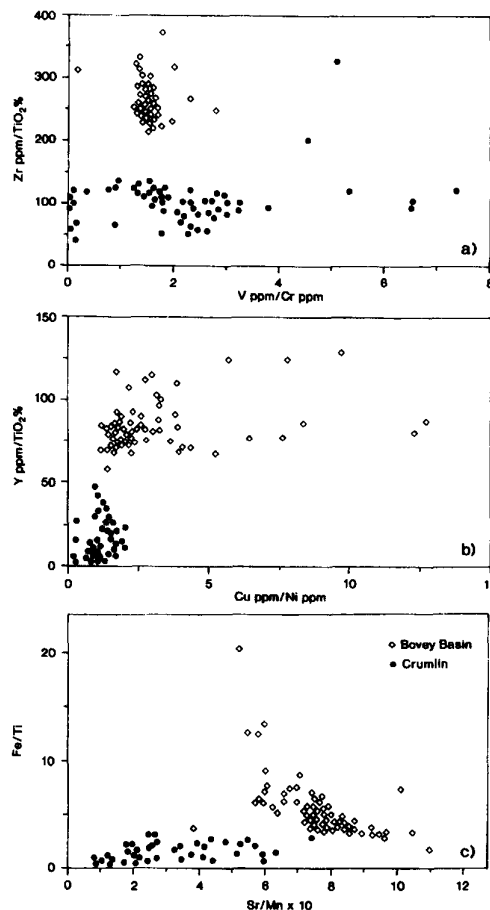

Figure 4: Element-element ratio plots for Bovey Basin and Crumlin sub-basin lignite samples indicating that the trace element composition of lignite from the two areas is characteristically different. (ALM=Aghnadarragh Lignite Member.)

Sharp weddellite peaks at 14.2° 2θ and 32.1° 2θ were not influenced by glycolation but broke down upon heating to 450°C. Kaolinite peaks were strongly asymmetric, suggesting disordering. It should be noted that no clay minerals occur in the southernmost sample analysed from the base of the Aghnadarragh Lignite Member. In this specimen quartz is the dominant phase, and has a peak height 200 times more intense than any quartz peak in other samples analysed.

Basalts of the Antrim Lava Group, which completely surround the Crumlin sub-basin, are deeply weathered in places. The first stage in the weathering of these rocks produced lithomarge, composed of a mixture of kaolinite and/or halloysite, and Fe-Ti oxides (McAlister *et al.*, 1988). Lateritization of this lithomarge produced gibbsite through decomposition of clays and loss of silica, although Fe-Ti oxides may have been relatively unaltered depending on the stage of weathering (Morad and Aldahan, 1986). The clay mineralogy of lignite samples from the Crumlin sub-basin is consistent with this material having been derived from weathered basalt.

TABLE 1: Mean values of trace elements determined by XRF on whole lignite from the Bovey Basin and the Crumlin sub-basin. BDL = below detection limit.

Area															
		%								ppm					
	TiO₂	Fe₂O₃	Ba	Cr	Cu	Mn	Nb	Ni	Rb	Sc	Sr	V	Y	Zn	Zr
Crumlin	1.001	1.400	156	62	36	155	BDL	41	BDL	11	38	140	BDL	22	100
Bovey	0.300	1.415	214	46	45	83	8	14	70	10	62	71	23	28	74
Detection limit	0.0002	0.0001	75	2	1	3	1	2	3	4	4	3	1	2	1

TABLE 2: Ash content-element concentration correlation coefficient data for lignites from a) the Bovey Basin and b) the Crumlin sub-basin. (ALM=Aghnadarragh Lignite Member)

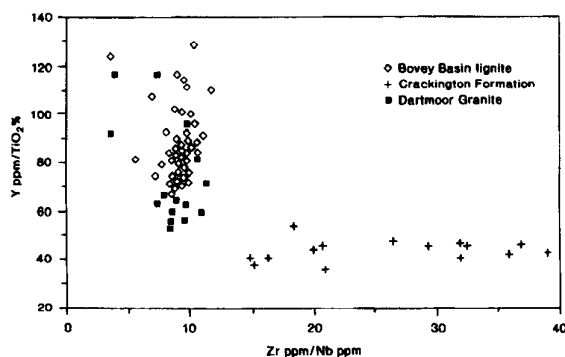| Area	Element													
	Ti	Fe	Ba	Cr	Cu	Mn	Nb	Rb	Sc	Sr	V	Y	Zn	Zr
Bovey Basin	0.925	-0.735	0.55	0.438	-0.439	-0.546	0.963	0.968	0.474	0.842	0.551	0.863	-0.447	0.921
ALM Top	0.21	0.454	0.065	0.457	0.381	0.208	0.115	0.193	0.326	-0.198	0.371	0.566	0.552	0.16
ALM Mid	0.035	0.068	0.224	0.206	0.377	0.133	-0.109	0.012	0.679	0.168	0.185	0.335	-0.052	0.041
ALM Base	0.803	0.405	-0.581	0.689	0.342	0.036	0.657	0.231	0.637	-0.324	0.665	0.558	0.138	0.632

Figure 5. Graph of Y/TiO$_2$ against Zr/Nb for lignite from the Bovey Basin and possible source rocks for the lignite inorganic fraction. Data for the Crackington Formation from Haslam and Scrivener, 1991. Data for the Dartmoor granite from Ward et al. 1992.
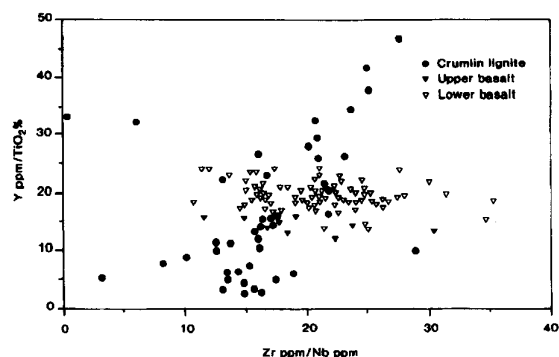

Figure 6. Graph of Y/TiO$_2$ against Zr/Nb for lignite from the Crumlin sub-basin and possible source rocks for the lignite inorganic fraction. Lignite data is from McCaffrey 1992 and basalt data is from Doherty 1983.

Detrital quartz in some of the lignites in the Crumlin sub-basin may have been derived from the Palaeozoic rocks of the Longford-Down Massif, which crops out to the south (McCaffrey, 1992).

Geochemistry

Lignite from the Bovey Basin has a characteristically different chemistry from that of lignite from the Crumlin sub-basin (Table 1). On average, Bovey Basin lignites have higher Cu, Rb, Y and Sr contents, whereas the Lough Neagh Group lignite contains higher concentrations of TiO$_2$, Cr, Mn, Ni, V and Zr. The average concentrations of Fe$_2$O$_3$, Ba, Sc and Zn in lignites from the two areas are similar. Plots of element ratios (which eliminated the need to normalise XRF data to ash content) are effective in discriminating between lignites from the two areas (Figure 4).

USE OF GEOCHEMICAL DATA IN PROVENANCE STUDIES

Ash:element correlation coefficients (Table 2) suggest that Y, Ti, Zr and Nb are still strongly associated with inorganic material in these lignites, indicating that the elements have not undergone significant mobilisation through solution during weathering, transport or deposition. Although element ratio plots do suggest possible source areas for inorganic detritus in lignites, they should ideally be used in conjunction with other provenance indicators (McCaffrey, 1992).

The basalts of the Antrim Lava Group are the most likely sources of inorganic detritus in the Crumlin sub-basin (McCaffrey, 1992). The Zr/Nb and Y/Ti ratios of the lignite samples from the Crumlin sub-basin are similar to those of samples of the basalts (Figure 5). Therefore there is some evidence that, under the conditions at the time of deposition, the values of these ratios in the lignite samples are similar to those of the bedrock in the source area.

Bovey Basin lignite samples have higher Y/Ti and lower Zr/Nb ratios than lignite samples from the Crumlin sub-basin. These differences in 'immobile element' ratios are likely to reflect differences in the chemistry of the respective source areas for the inorganic fractions of the lignites. In samples from the Dartmoor granite, values of Y/Ti are higher and Zr/Nb lower than in the basalts of the Antrim Lava Group, whereas Dartmoor granite samples have similar Y/Ti and Zr/Nb ratios to Bovey Basin lignite

samples (Figure 6). In contrast, the rocks of the Crackington Formation have Y/Ti and Zr/Nb ratios which are dissimilar to those of the Bovey Basin lignite samples.

From this evidence it is reasonable to conclude that the Dartmoor granite is a plausible main source for the inorganic detritus in the lignites in the Bovey Basin, and that the rocks of the Crackington Formation are unlikely to have made more than a minor contribution.

DISCUSSION

Using both mineralogical and geochemical evidence it has been shown that the inorganic fraction of organic rocks in the Bovey Basin and the Crumlin sub-basin reflects the geology of the surrounding rocks to a high degree. The evidence suggests that a granitic source dominated detrital input to the Bovey Basin at the time of lignite formation, and that the input of locally weathered sedimentary rocks was minor.

In this paper the inorganic fraction of a single lignite horizon sampled in the Newbridge Quarry in the Bovey Basin has been shown to be dominated by a Dartmoor granite source. However, as other authors have noted (see above) the question of the source of the rest of the infill of the Bovey Basin is complex and the provenance of other horizons in the Bovey Basin may vary. Indeed, it is possible that the provenance of the inorganic fraction of a single lignite horizon will vary over its area, and if sampled in a different locality will contain mineral matter deposited by different drainage systems, draining different rocks. The question of the detailed provenance of Bovey Basin rocks is far from resolved.

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