

Applied & Environmental Geochemistry 2025

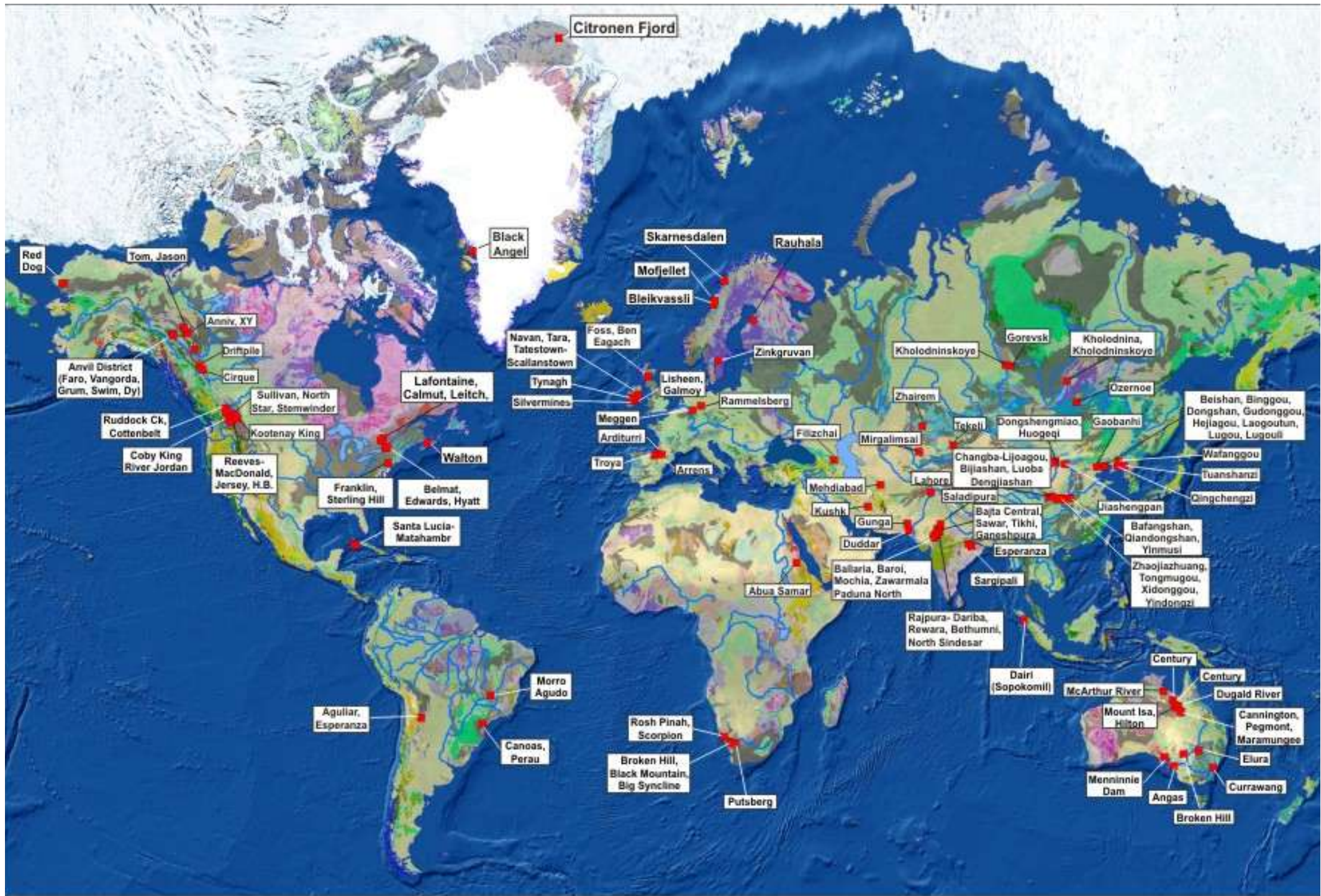
Sea-floor poly-metallic massive sulphides and application of the alteration index

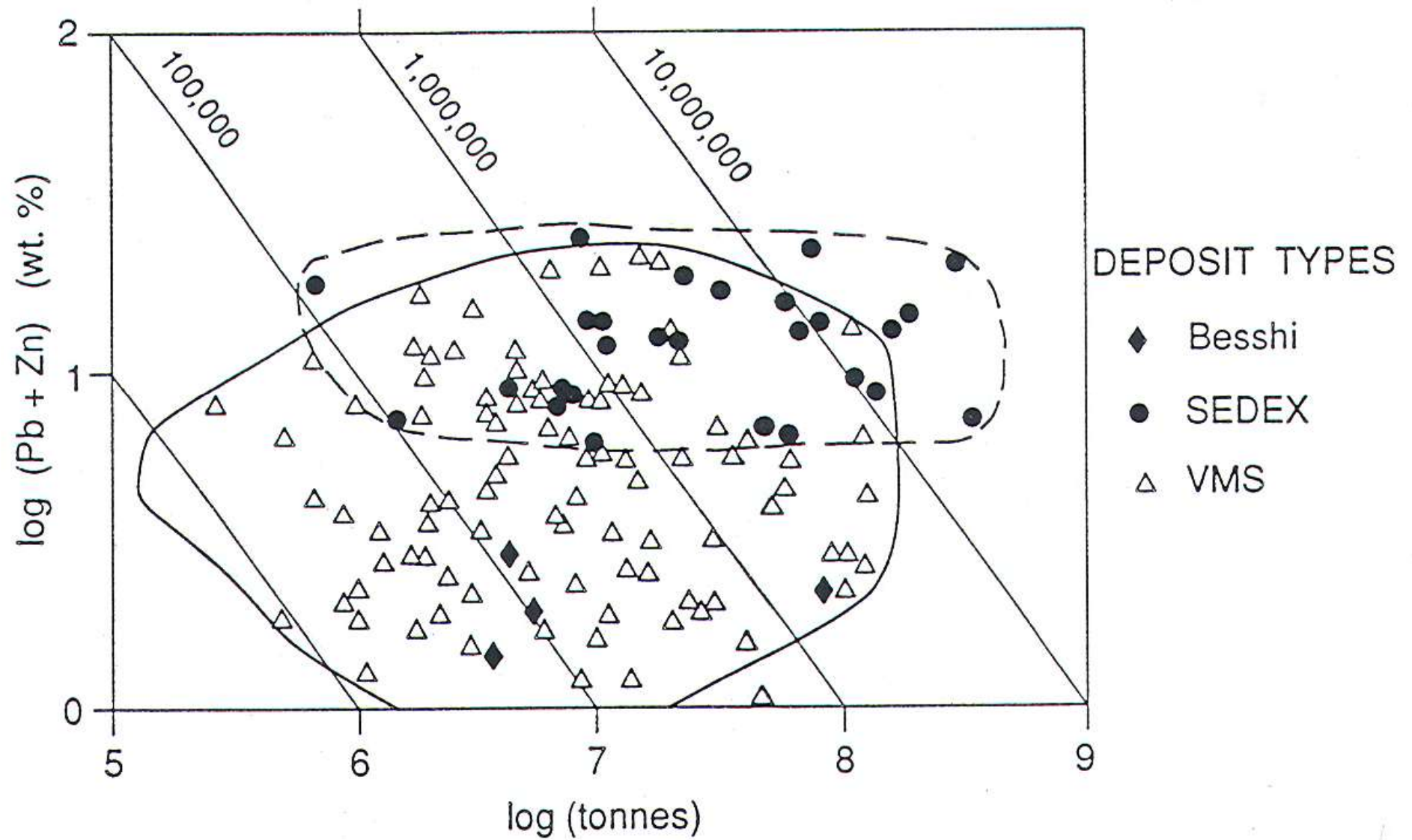
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Sedimentary-exhalative (SEDEX) deposits

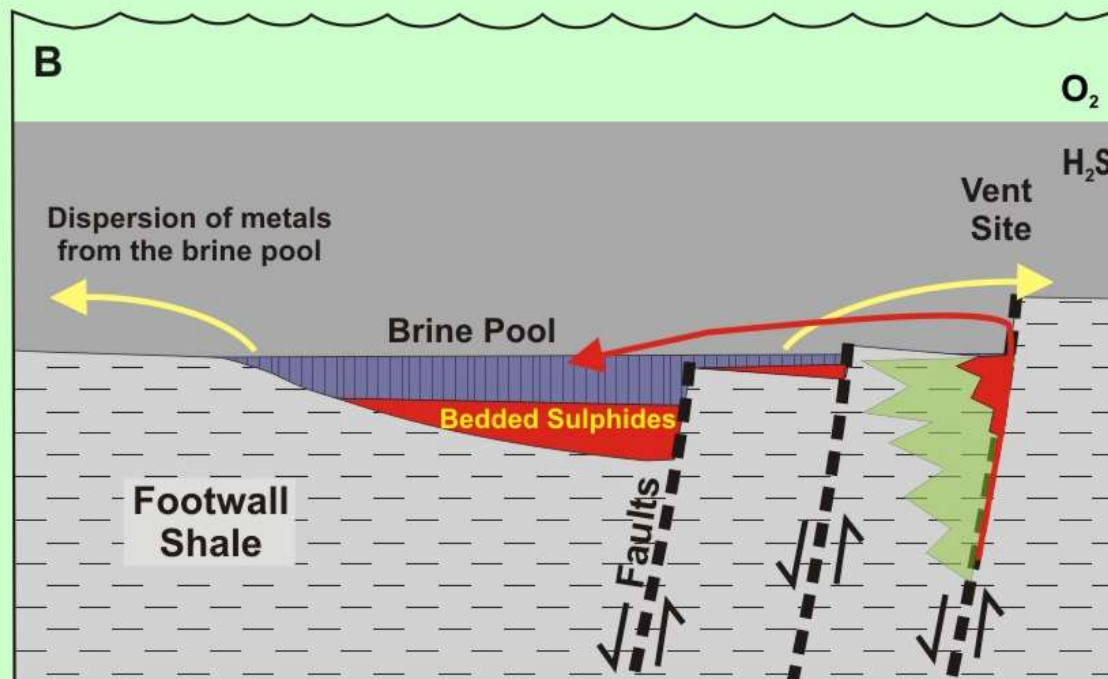
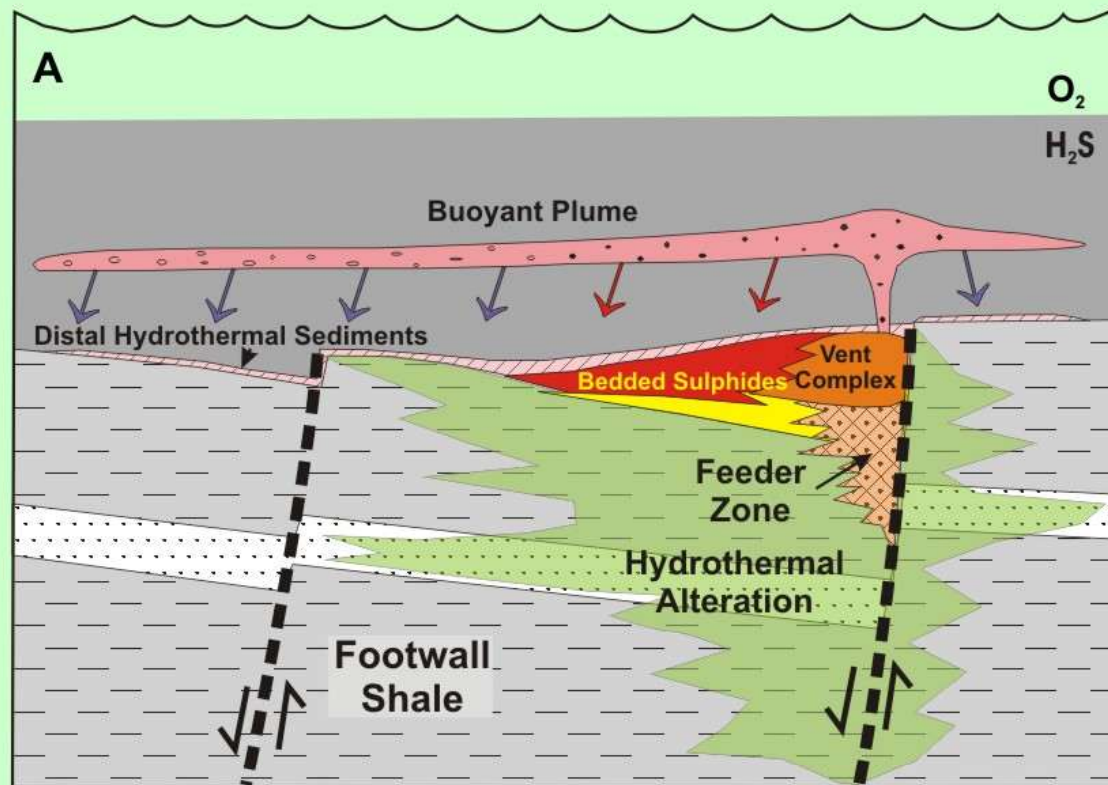
- SEDEX deposits contain more than half of the world's known resources of Pb and Zn and are generally represented by bigger and richer (albeit fewer) deposits than the VMS class.
- They are typically formed within rifted continental margins or intra-cratonic rift basins, and are hosted by marine clastic or chemical sediments with little or no direct association with volcanic rocks.
- Most major SEDEX deposits are Palaeo- to Mesoproterozoic in age, e.g. MacArthur River (“HYC”), Mount Isa and Broken Hill (Australia), Sullivan (Canada) and Aggeneys-Gamsberg (South Africa). Palaeozoic examples include Red Dog (Alaska), Tom & Jason (Canada), Navan (Ireland), Meggen-Rammelsberg (Germany), amongst others.





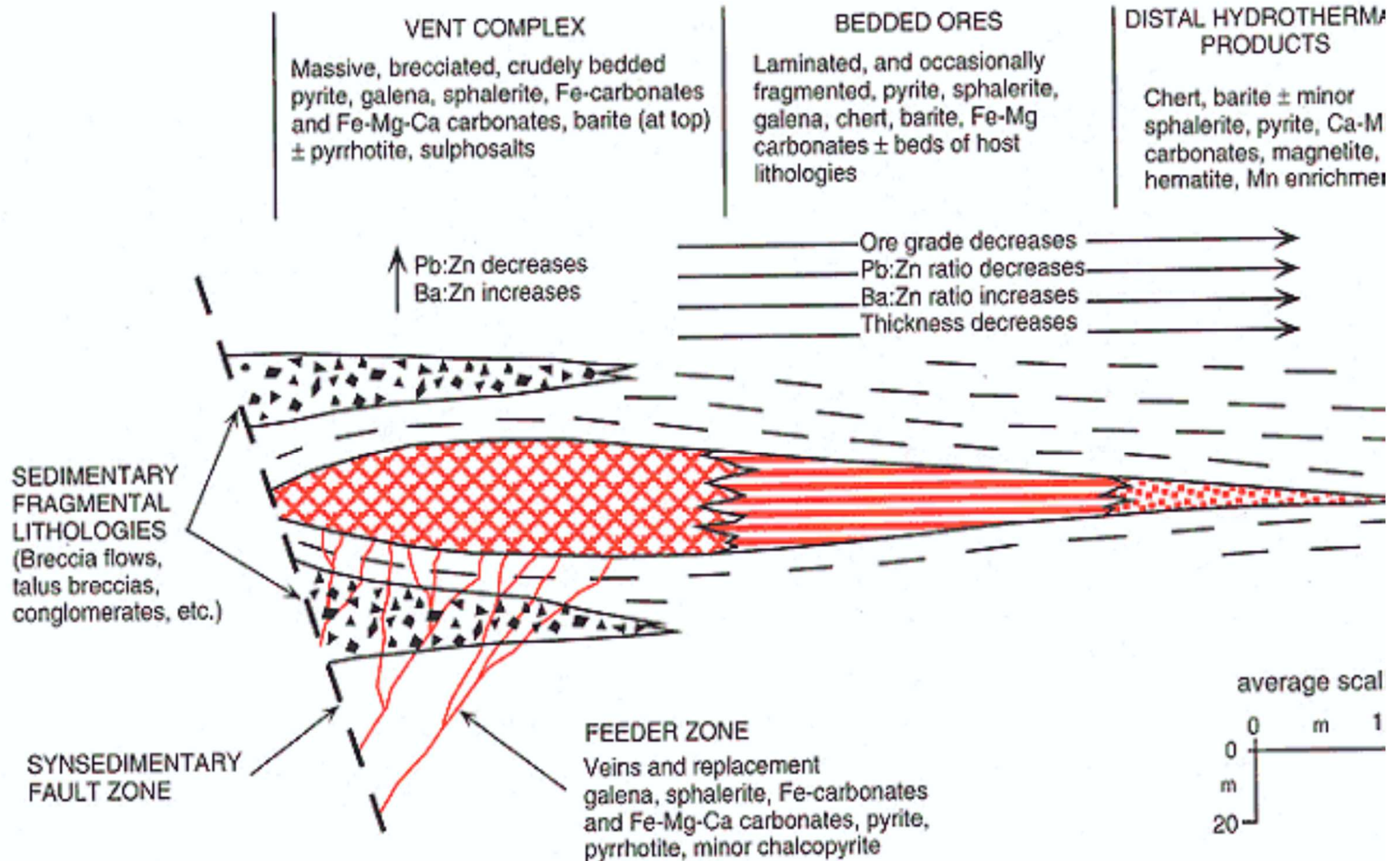
SEDEX deposits: general points

- SEDEX deposits are considered to have formed by the precipitation of sulfide minerals from warm (generally between 150 to 300°C), saline fluids (brines derived from essentially evolved seawater) discharged into the sea through fractures in the seafloor.
- The resultant deposits are large and commonly internally layered, with sulfide-rich beds inter-layered with sulfide-poor ones.
- A significant feature of some SEDEX deposits is the so-called feeder pipe, i.e. the zone of reaction between up-flowing hydrothermal fluids and footwall sediments.
- SEDEX deposits underlain by a feeder pipe would represent *vent-proximal* ores; by contrast, those which are spatially disconnected from the feeder zone would be called *vent-distal*.



General characteristics of SEDEX ores

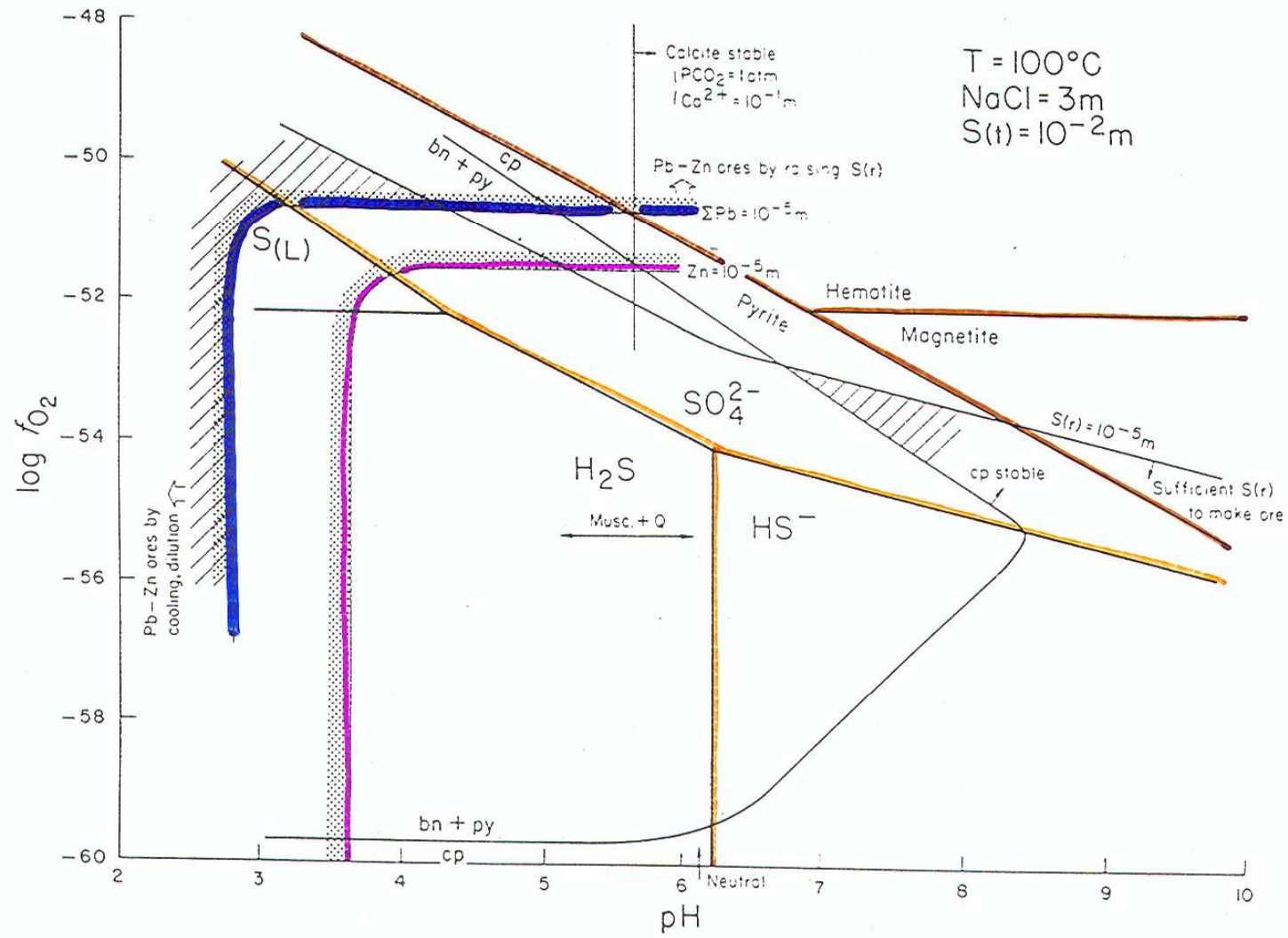
- Stratiform mineralization (typically of a high aspect ratio);
- Stacked lenses of massive sulfide ore:
 - thin, highly continuous laminations of galena-sphalerite-pyrite (+Ag and occasionally Au, but little or no Cu) conformably bedded with host rocks;
 - outer margin of bedded hydrothermal products (barite, Fe-Mn carbonates, chert, apatite, etc);
 - footwall zone of minor stockwork associated with hydrothermal alteration = alteration pipe;
- Strong lateral (and to a much lesser extent vertical) zonation;
- Spatial association with a syn-sedimentary fault system.



Schematic illustration of the characteristic features of the idealized Sedex deposit.

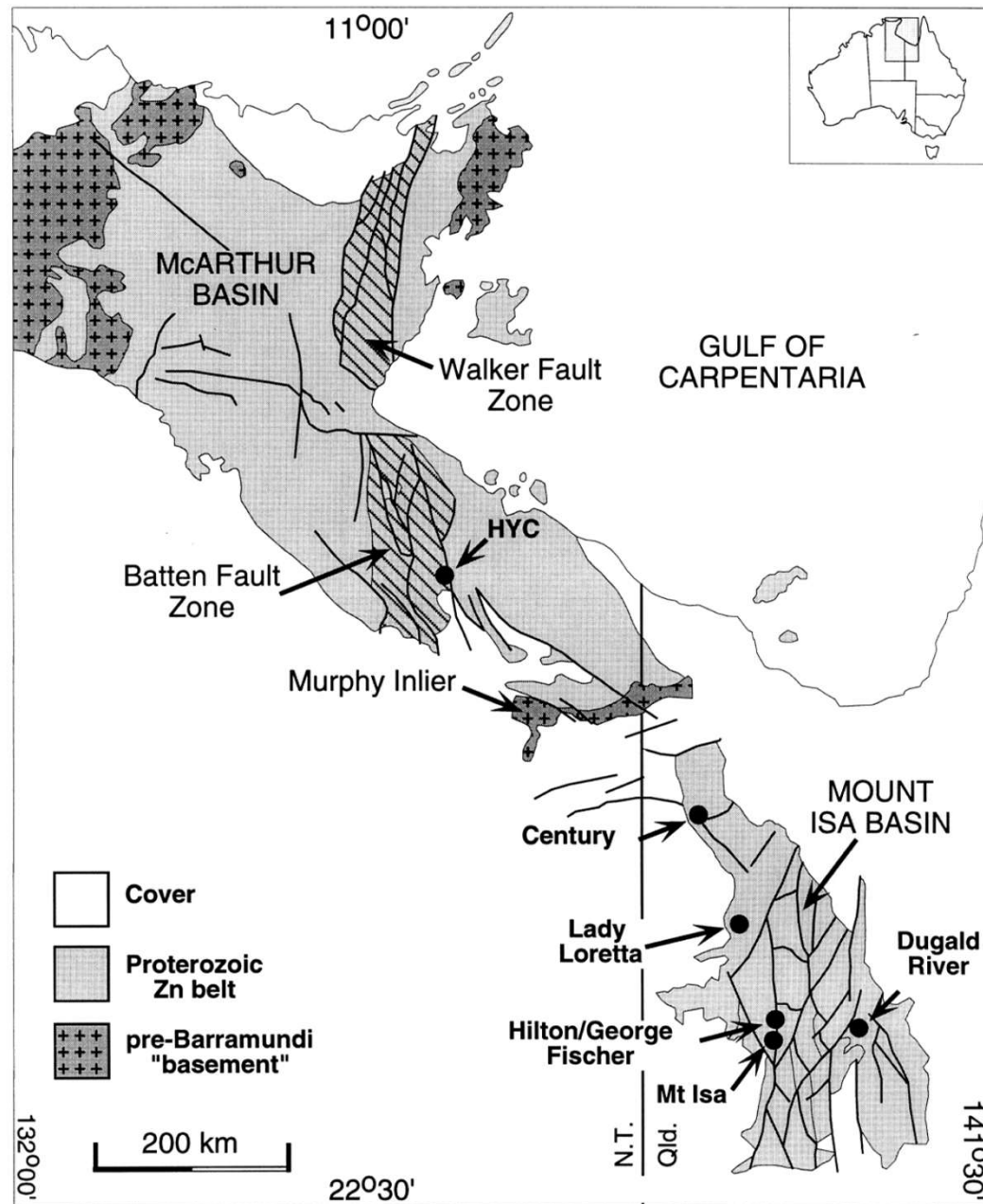
Oxidized or reduced metalliferous brines?

- The two discrete brine types capable of transporting Zn & Pb are oxidized brines (SO_4^{2-} -predominant) and reduced, acidic brines (H_2S -predominant). *McArthur-type* deposits (e.g., McArthur River, Mount Isa) precipitate from oxidized, acidic to near-neutral brines that evolve from sedimentary basins dominated by carbonates, evaporites and hematitic sandstones and shales. Selwyn-type deposits (e.g., Sullivan, Rammelsberg, deposits of the Selwyn basin in Canada) precipitate from acidic, reduced connate brines that evolved in reduced siliciclastic and shale basins.
- Temperature decrease and dilution (fluid mixing), addition of H_2S and pH increase can all be effective depositional processes for Zn and Pb from reduced brines. In contrast, sulfate reduction and/or addition of H_2S (via fluid mixing or interaction with earlier formed pyrite) may be the important processes for sphalerite and galena deposition from oxidized brines.



Ancient SEDEX deposits: McArthur River (“HYC”), North Australian Zinc Belt

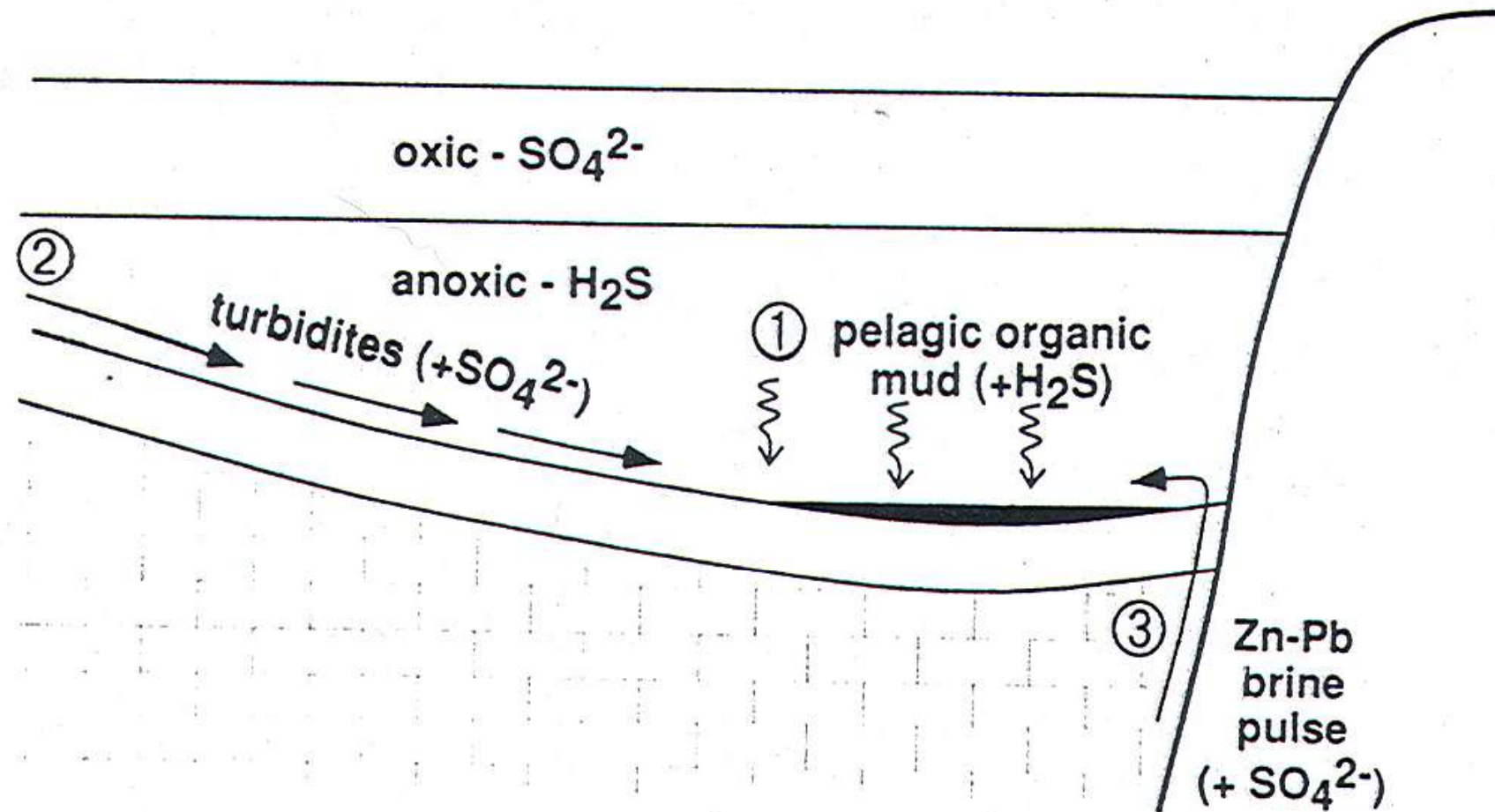
- The Paleoproterozoic McArthur basin (180,000 km²) and the stratigraphically equivalent Mount Isa basin (70,000 km²) are exposed in central northern Australia. Between them, they host most of the world’s known Proterozoic SEDEX deposits (HYC, Mount Isa, Hilton, George Fischer, Century, Dugald River, Lady Loretta), forming the Australian Proterozoic “zinc belt”.
- The MacArthur River (HYC) deposit is a large tonnage, high grade Zn-Pb SEDEX deposit (237 Mt @ 9.2% Zn, 4.1% Pb, 41 g/t Ag, and 0.2% Cu), comprising one of seven major stratiform sediment-hosted deposits of the Proterozoic North Australian zinc belt.
- The deposit consists of eight stratiform ore lenses near the base of a thickened section of the host carbonaceous siltstones, the *Barney Creek Formation*.



Australian Proterozoic zinc belt, showing locations of the major sedex deposits and the key geologic elements of the region.

McARTHUR GROUP	BATTEN SUBGROUP	LOOKING GLASS FM	AMOS FORMATION
		STRETTON SANDSTONE	
		YALCO FORMATION	
		LYNOTT FORMATION	Donnegan Member Hot Spring Member Caranbirini Member
	UMBOLOOGA SUBGROUP	REWARD DOLOMITE	
		BARNEY CREEK FORMATION	HYC Pyritic Shale Mb. W-Fold Shale Mb. Cooley Dolomite Mb.
			Coxco Dolomite Member
		TEENA DOLOMITE	
		EMMERUGGA DOLOMITE	Mitchell Yard Dolomite Member Mara Dolomite Member
		MYRTLE SHALE	
		LEILA SANDSTONE	
		TOOGANINIE FORMATION	
		TATOOOLA SANDSTONE	
		AMELIA DOLOMITE	
		MALLAPUNYAH FORMATION	
		MASTERTON SANDSTONE	

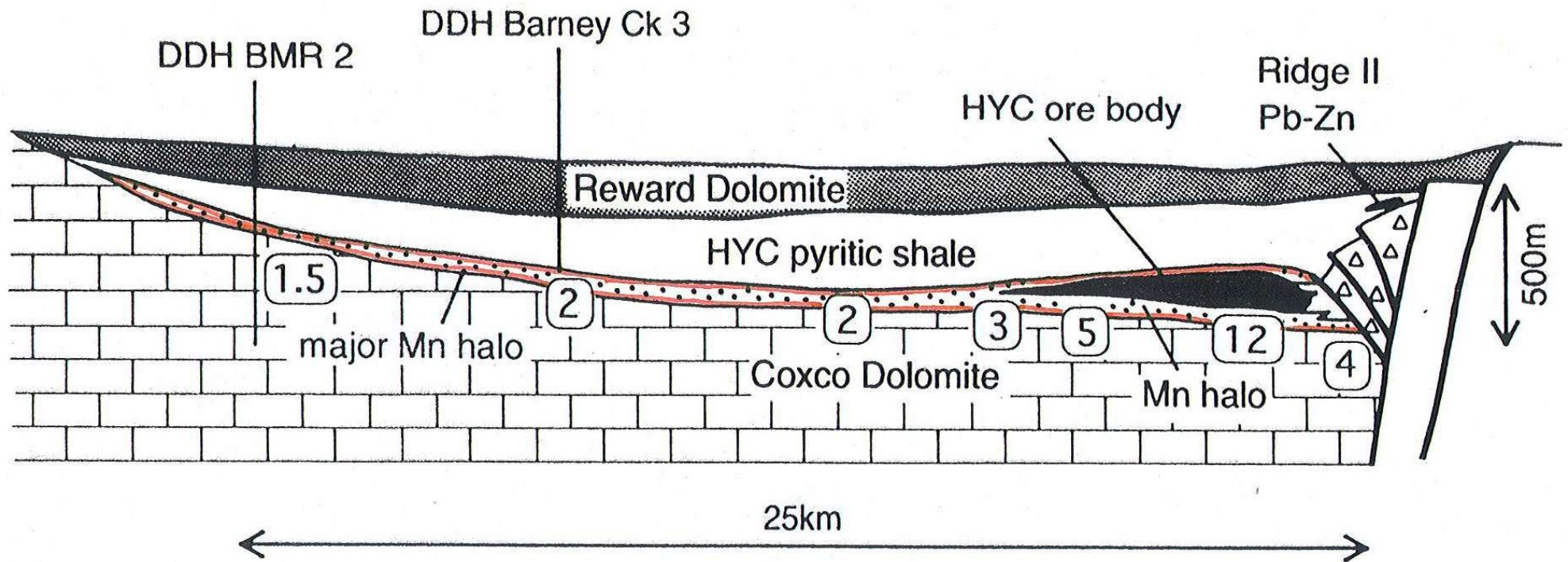
Stratigraphic column of the southern McArthur basin (modified after Pietsch et al., 1991).



Diagrammatic representation of the three proposed components of deposition during ore formation at HYC. (1) Pelagic mud from anoxic water column; (2) oxic quartz-carbonate turbidity flows from the basin margins; (3) Zn-Pb-bearing brine pulses migrating along active proximal faults.

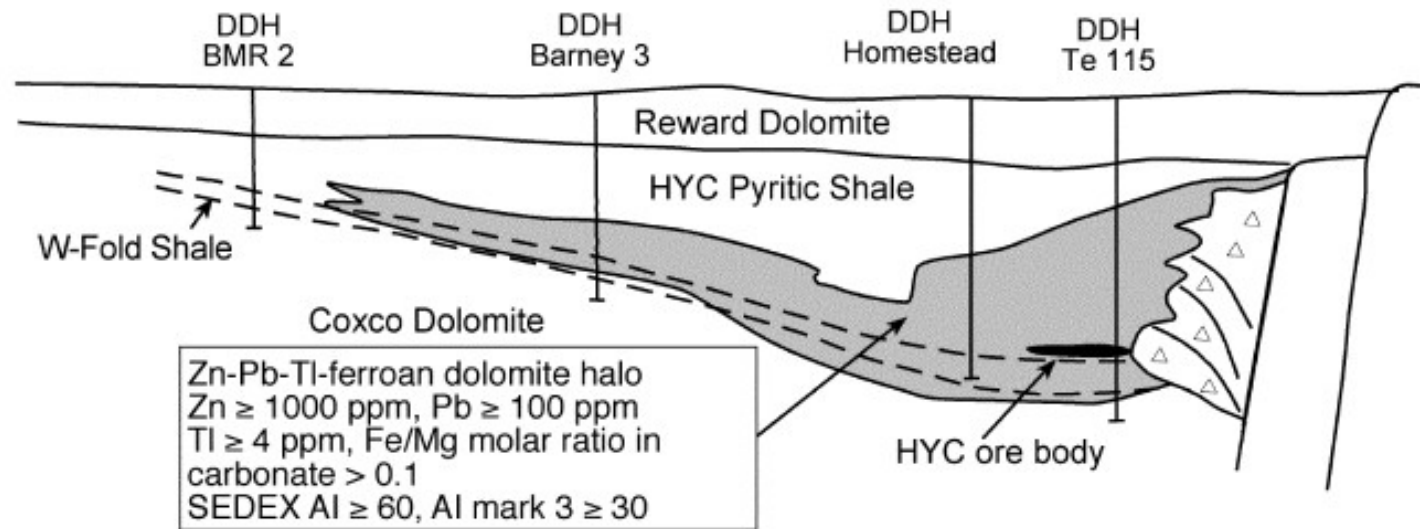
Geochemical halo around the HYC

- Carbon and oxygen isotope ratios in fine-grained sedimentary dolomite in the Barney Creek Formation demonstrates the presence of an extensive isotope halo surrounding the giant stratiform HYC Zn-Pb-Ag deposit. Dolomite within the halo shows an ^{18}O -enriched and ^{13}C -depleted isotope signature ($\delta^{18}\text{O} = 23$ to 26‰ SMOW, $\delta^{13}\text{C} = -2$ to -3.5‰ PDB), relative to normal Proterozoic sedimentary dolomite beyond the halo ($\delta^{18}\text{O} = 20 - 23\text{‰}$ and $\delta^{13}\text{C} = 0$ to -2‰).
- The C-O isotope halo within the dolomitic siltstones extends at least 15 km southwest of the HYC deposit and approximately coincides with a previously defined litho-geochemical halo of elevated Fe, Mn, Zn, Pb, and Tl. Dolomitic siltstone lamellae within the stratiform Zn-Pb-Ag ores at HYC exhibit an isotopic range similar to that of the halo dolomites, suggesting that the ore and halo equilibrated with the same hydrothermal fluid.

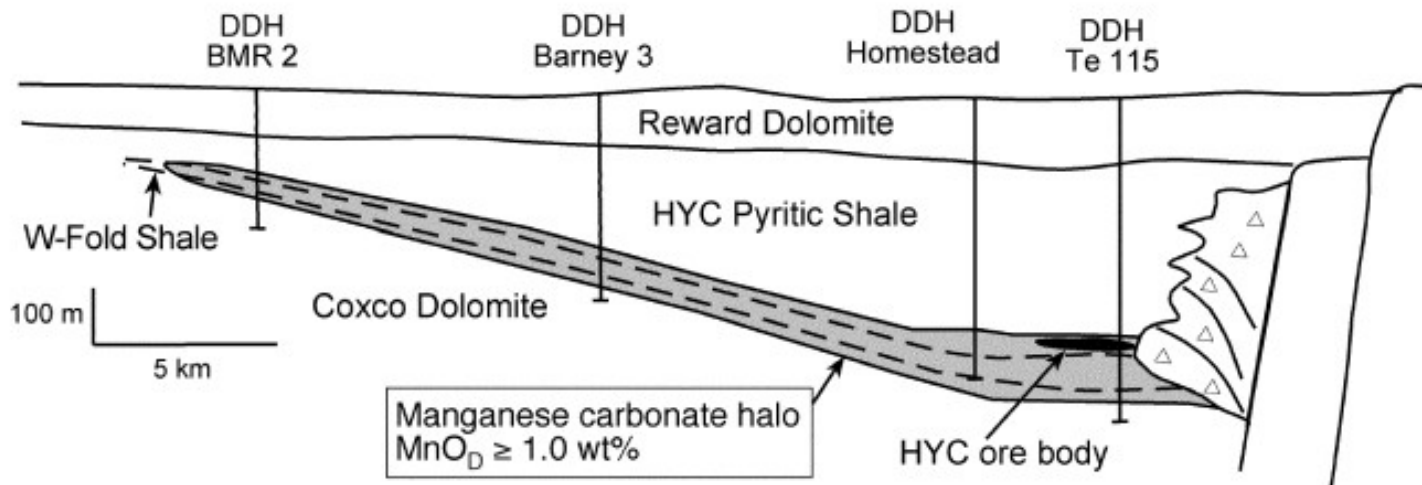


Reconstruction of the manganese halo related to the HYC deposit, interpreted from drill hole analyses in Corbett et al. (1975), plus additional data from this study. The numbers in the boxes are the maximum value of wt percent MnO in dolomite in the W-Fold Shale, determined from the whole-rock analyses, calculated using the procedure of Large and McGoldrick (in press).

a. Ferroan dolomite halo



b. Manganese carbonate halo



Lithogeochemical halo model for the HYC deposit from Large et al. (2000). $\text{AI mark 3} = 100(\text{FeO} + 10 \text{ MnO})/(\text{FeO} + 10 \text{ MnO} + \text{MgO} + \text{Al}_2\text{O}_3)$, $\text{MnO}_D = \text{MnO} \times 30.41/\text{CaO}$, $\text{SEDEX AI} = 100(\text{FeO} + 10 \text{ MnO})/(\text{FeO} + 10 \text{ MnO} + \text{MgO})$.

Origin of the geochemical halo around HYC

- It has been proposed that the halo dolomites would have equilibrated with low-temperature fluids (50° - 120°C), which were enriched in ^{18}O ($\delta^{18}\text{O} = 5 \pm 5\text{‰}$) but with an average crustal carbon isotope signature ($\delta^{13}\text{C} = -6 \pm 1\text{‰}$). The oxygen and carbon isotope halo would be related to the development of an extensive brine pool. This pool was deepest in the vicinity of the HYC deposit adjacent to a feeder fault and it became shallower to the southwest away from the fault.
- Using the carbon isotope fractionation equation between dolomite and HCO_3^- , the temperature variation can be estimated at the base of the brine pool during accumulation of the Barney Creek Formation. Brine pool temperatures were highest in and adjacent to the deposit (40°–70°C) and decreased to values of 17° to 30°C remote from the deposit. These temperatures are similar to those recorded in the Red Sea brine pool associated with the Atlantis II metalliferous sediment deposit.

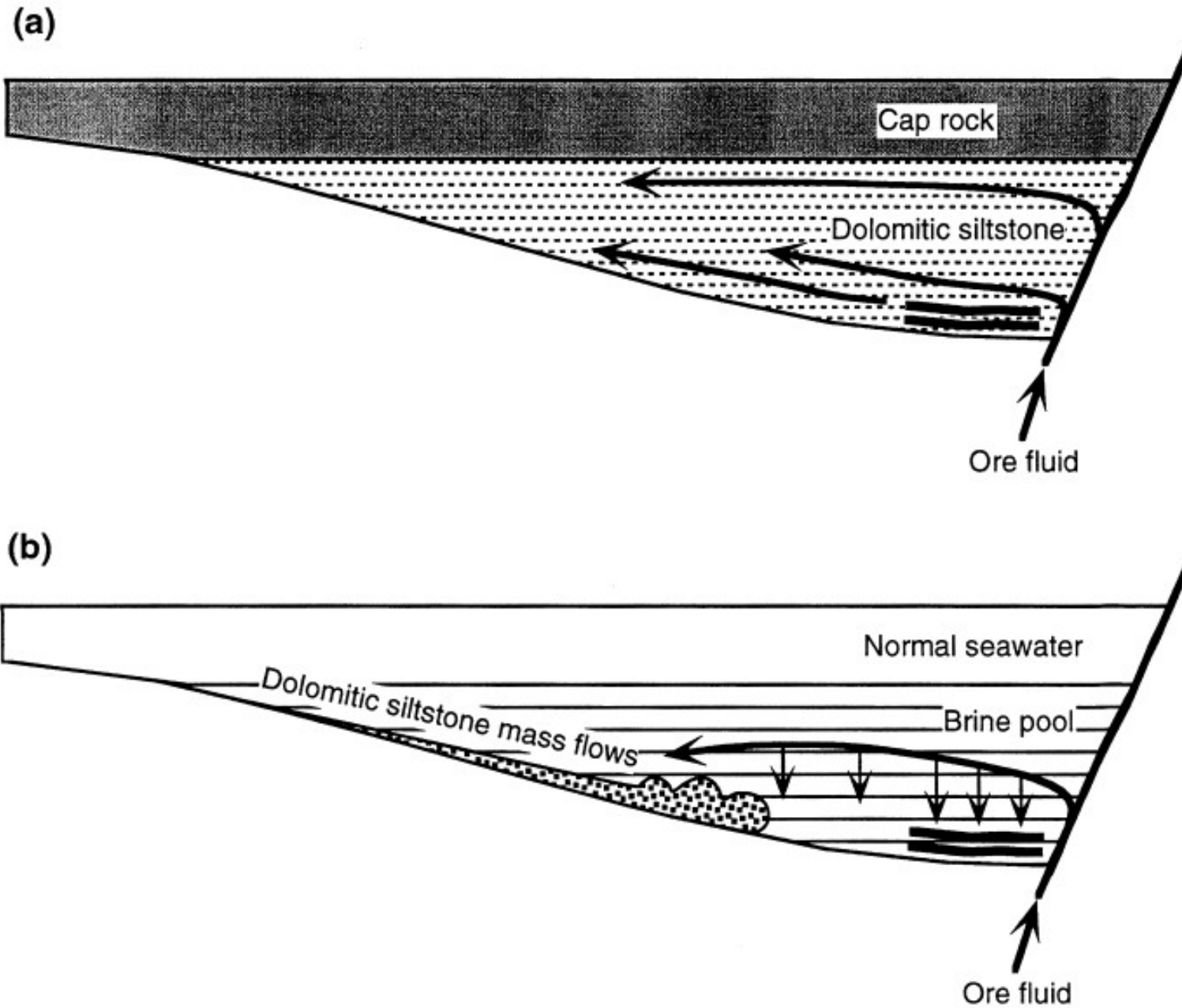
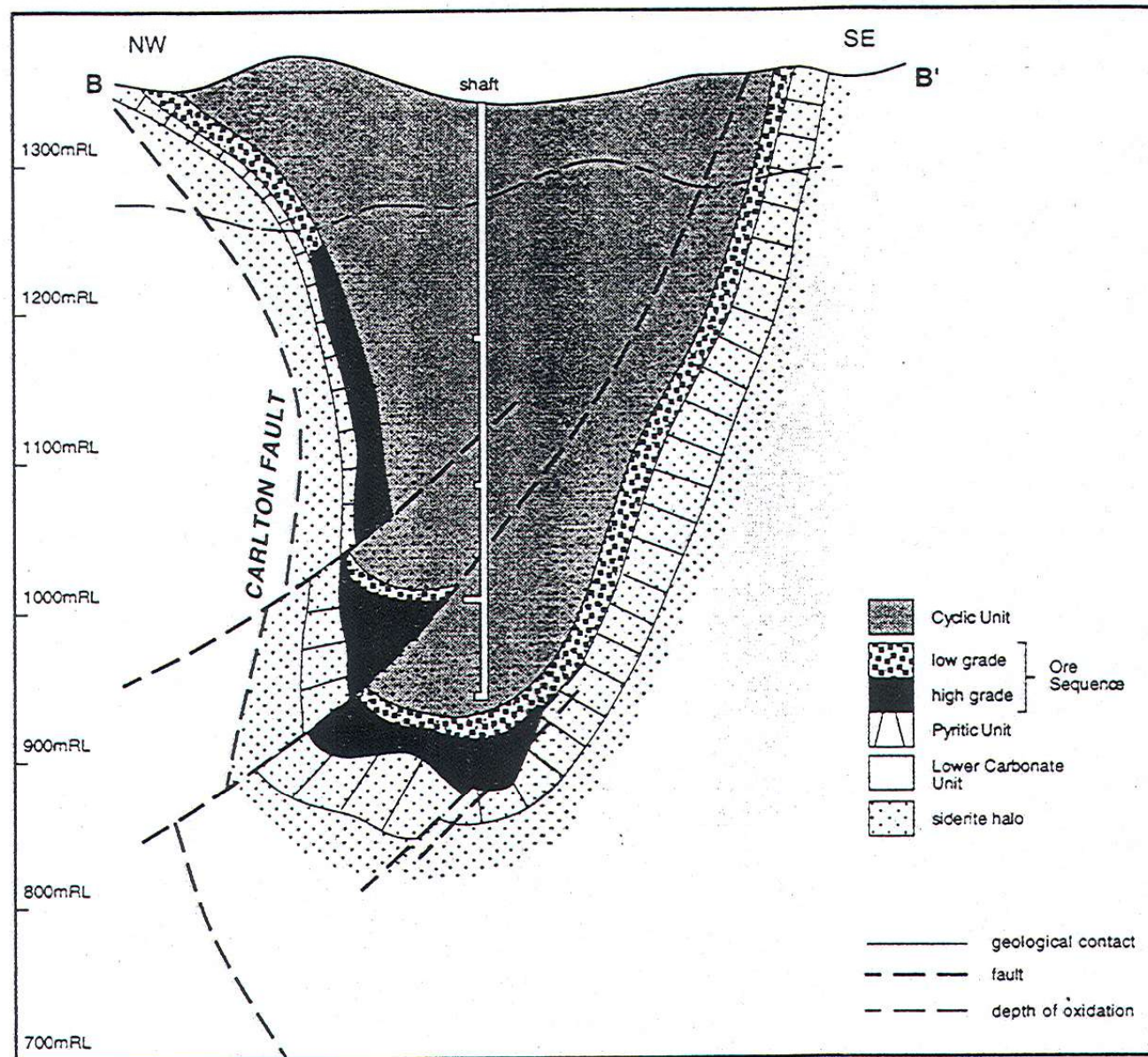
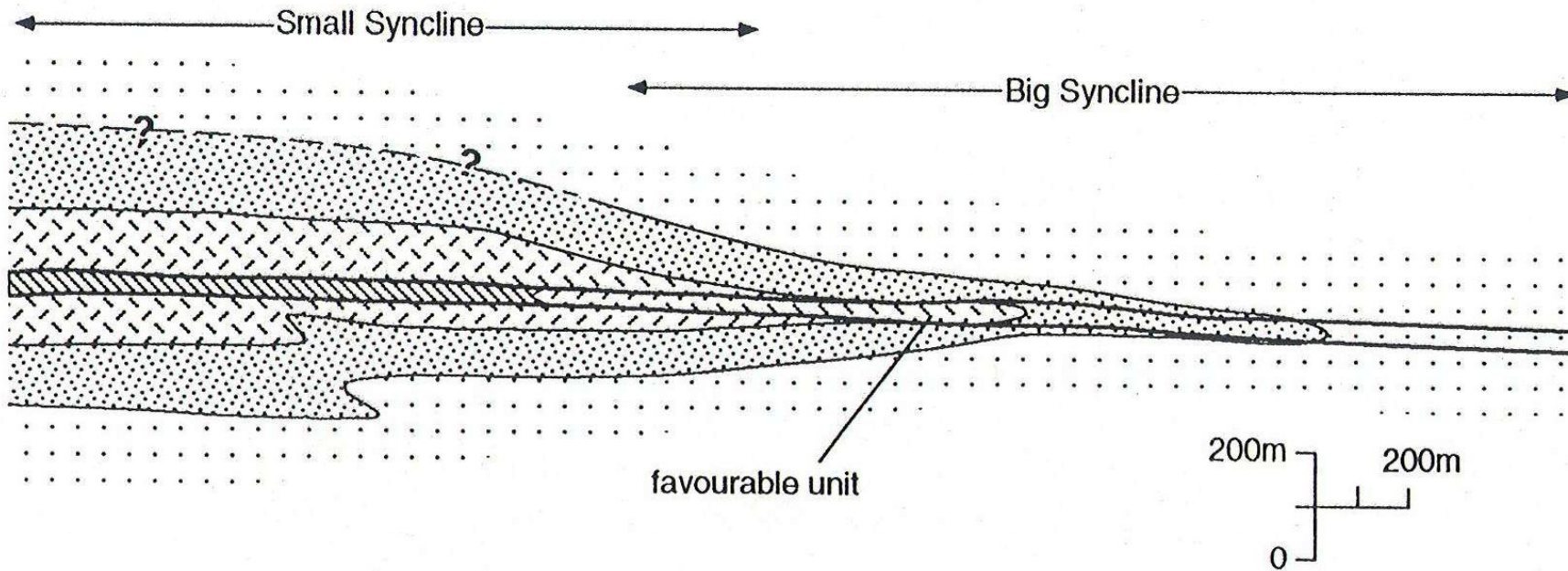






Figure 1. Cross section depicting HYC lithogeochemical and isotope halo formation. a) Replacement below the basin floor. b) Exhalation on the basin floor.



Typical geological cross section, Lady Loretta deposit (section 2300), modified from Hancock and Purvis (1990) and Carr (1984).

LADY LORETTA HALO MODEL



		Zn	Pb ppm	dominant Carbonate	Tl ppm	MnO %	CaO %	SEDEX AI	MnO _d /s %	Metal Index
Zn-Pb ore		>5%	>1000	siderite	>50	0.1-0.4	0-1	80-100	1-10	>8x10 ⁴
Siderite halo		100ppm to 5%	10-1000	siderite	2-50	0.01-1	0-1	60-100	1-10	2x10 ³ -3x10 ⁴
Ankerite halo		20-200ppm	<70	ankerite	2-50	0.01-0.04	1-2	38-60	0.4-0.7	2-7x10 ³
Dolomite halo		<30ppm	<20	dolomite	<2	<0.01	5-10	10-40	<0.3	<3x10 ³

Halo model (pre-folding) for the Lady Loretta deposit based on geochemical data from the Small Syncline and Big Syncline.

Time distribution of SEDEX deposits

- The concentration of sulphate prior to 2.4Ga is believed to have been less than 1% of that in modern seawater. This implies that the concentration of H₂S in Archean euxinic basins was also much lower than today, and that the occurrence of sulfate minerals in marine evaporites would have been vanishingly small. Hence the concentration of sulphate in brines associated with Archean evaporites would also have been extremely small.
- The foregoing would explain the apparent absence of SEDEX deposits before the “Great Oxidation Event (GOE)” of Holland (2005), i.e. the sharp rise in atmospheric oxygen at ca. 2.4Ga. Also, the solution transport of the quantities of Pb, Zn, Cu, and Ag in SEDEX deposits at their relatively low T of deposition (<250°C) requires the virtual absence of reduced S in the circulating brines. Such relatively oxidized solutions were probably more common after than before the GOE.

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