

# On the composition, distribution and genesis of continental oxidate sediments

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## Introduction

The term oxidate sediments was introduced by Goldschmidt (1954, p. 639-641) for sediments formed by oxidation of solute ferrous and manganese ions to the tri- and quadrivalent state, respectively. Oxidate sediments can be grouped into continental (freshwater) and marine (salt water) varieties. The continental type, which is treated here, occurs as coatings, crusts and nodules in soils, springs, bogs, lakes and streams. Such deposits were referred to very early in the literature (e.g. Vogt 1906), due to their utilisation in the production of bloomery iron (Espelund 1991). Oxidate sediments can be efficient sinks for heavy metals others than Fe and Mn. This has been regarded as a problem in geochemical exploration, because varying amounts of Fe and Mn oxides in stream sediments may cause heavy metal anomalies that are not related to mineralisation (Ottesen & Theobald 1994). However, the scavenging effect may also be taken as an advantage in geochemical exploration, since it indicates that oxidate sediments may be sensitive indicators of heavy metals.

Although the formation of secondary oxides of Fe and Mn has long been considered to be a very important geochemical process (Goldschmidt 1954, p. 639-642), the present knowledge about oxidate sediments is rather incomplete. This contribution reviews some data recently obtained by NGU (Ottesen & Volden 1983, Ottesen et al. 1985, 1994, Bølviken et al. 1994, Ottesen & Kjeldsen 1986, and Kjeldsen et al. 1994).

## Materials and methods

125 samples of oxidate sediment nodules, crusts and coatings were collected from stream beds and lake bottoms in southeastern Norway. The samples were analysed for up to 52 chemical elements by a variety of methods. Mineral components were identified in 33 of the samples by

X-ray diffraction spectrometry and microprobe backscattered electron image and secondary electron image analysis. Carbon-14 dating was performed on 2 samples.

## Results

### Composition and age of oxidate sediments

The main Fe minerals are goethite ( $\alpha$ -FeO(OH)), ferrihydrite ( $\text{Fe}_5\text{O}_7(\text{OH})4\text{H}_2\text{O}$ ), lepidocrocite ( $\gamma$ -FeOOH) and hercynite ( $\text{FeAl}_2\text{O}_4$ ). The main Mn minerals are vernadite ( $\text{MnO}(\text{OH})_2$ ) and birnessite ( $\text{Na}_4\text{Mn}_{14}\text{O}_{27}9\text{H}_2\text{O}$ ). Al-bearing silicates and psilomelane ( $(\text{Ba},\text{H}_2\text{O})\text{Mn}_8\text{O}_{16}$ ) occur as minor minerals. Amorphous substances containing Fe, Mn, C, Al and Si are intermixed with each other and with the minerals.

Table 1 shows that a variety of chemical elements occur in wide concentration ranges in oxidate sediments. Depending on location, the elements are enriched or depleted relative to their

Table 1. Contents of hydrochloric acid-soluble elements in oxidate sediments, Norway, and average enrichment factors relative to the total contents in granites (Vinogradov 1962).

| Element  | Arithm. mean | Range        | N   | Enrichment factor |
|----------|--------------|--------------|-----|-------------------|
| Al (%)   | 2.1          | 0.4 - 7.9    | 114 | 0.3               |
| As (ppm) | 27.5         | 1 - 110      | 109 | 18                |
| Ba (ppm) | 2973.7       | 29 - 31390   | 114 | 4                 |
| Cd (ppm) | 16.4         | <1 - 58      | 110 | 164               |
| Co (ppm) | 163.0        | <1 - 1170    | 112 | 33                |
| Cr (ppm) | 26.0         | 2 - 130      | 114 | 1                 |
| Fe (%)   | 13.2         | 2.3 - 54.9   | 114 | 5                 |
| K (%)    | 0.05         | 0.002 - 0.42 | 95  | 0.02              |
| La (ppm) | 85.1         | 8 - 470      | 114 | 1                 |
| Li (ppm) | 16.9         | <1 - 85      | 84  | 0.4               |
| Mg (%)   | 0.15         | 0.01 - 1.1   | 114 | 0.3               |
| Mn (%)   | 10.3         | 0.02 - 26.1  | 114 | 172               |
| Mo (ppm) | 174.6        | <1 - 940     | 87  | 175               |
| Ni (ppm) | 121.4        | <2 - 870     | 113 | 15                |
| Pb (ppm) | 33.6         | 2 - 900      | 92  | 2                 |
| Sr (ppm) | 34.2         | <1 - 280     | 112 | 0.1               |
| Th (ppm) | 19.2         | <6 - 85      | 80  | 1                 |
| U (ppm)  | 269.1        | <20 - 650    | 98  | 77                |
| V (ppm)  | 48.3         | 13 - 500     | 114 | 1                 |
| W (ppm)  | 24.9         | <2 - 110     | 110 | 63                |
| Zn (ppm) | 1220         | 24 - 5960    | 114 | 28                |

normal contents in granites (Vinogradov 1962). For the HCl soluble fraction of the trace elements, the four highest average enrichment factors are 175 (Mo), 164 (Cd), 77 (U) and 63 (W). Maximum enrichment factors for single values may be up to five times higher. These results confirm that determination of the contents of trace elements in samples of oxidate sediments can be used as a sensitive method in regional geochemical exploration.

Stream nodules from the northern Oslo Graben were found to have an age of  $1220 \pm 120$  years B.P., while corresponding figures for concretions from lake Storsjøen in the Solør region were  $2760 \pm 200$ .

### Geographical distribution of oxidate sediments

Occurrences of oxidate sediments tend to cluster within large provinces. In agreement with earlier observations (Vogt 1906, Ljungren 1953, 1955, Ottesen & Volden 1983, Ottesen et al. 1985) such provinces in Norway were found to be associated with granites and other acidic rocks. Moreover, our observations indicate that oxidate sediment-bearing granites are in general magnetic and connected with major tectonic zones. The Oslo Graben and the Protogene zone in Solør (Gaal & Gorbatshev 1987) are outstanding examples of such granites.

### Suggested genesis of oxidate sediments

Local occurrences of oxidate sediments will form in situations such as that indicated in Fig. 1. Due to low redox potential (Eh) in a bog,  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  (which both are ubiquitous at the Earth's surface) are reduced to the more soluble forms  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . When entering water with higher Eh and higher pH further downstream, the dissolved bivalent ions are reoxidised to the less soluble forms, which are precipitated onto material in the stream bed. Organic matter in the bog is the reducing agent, while air in the stream water is the oxidation agent.

We suggest that the formation of all types of oxidate sediments follows the same sequences, namely 1) reduction of  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ , 2) dissolution of the bivalent ions and subsequent migration, and 3) reoxidation and precipitation if the dissolved species encounter oxidising environments. The ultimate oxidation agent will be atmospheric oxygen. The reducing agent will vary with the circumstances; the existence of oxidate sediment provinces implies that it must be active over large areas. The following five alternatives for such reducing agents fulfil this requirement:

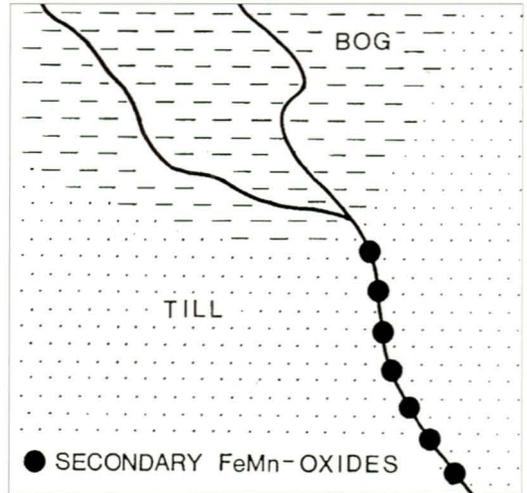


Fig. 1. Formation of oxidate sediments in a stream that is aerated after draining a bog area.

1) *Organic matter in bogs.* In regions with a temperate climate, bogs may be very frequent and extensive. Their reducing effect is illustrated in Fig. 1.

2) *Sulphide mineralisations.* Sulphides of Fe and other heavy metals occur both locally and regionally as disseminations or massive layers in several types of bedrock. Such reducing minerals may also have been brought into the overburden by mechanical processes.

3) *Carboniferous black shales.* Occurrences of Carboniferous black shales are common over large areas in a variety of geological environments. These shales have reducing properties due to their high contents of C and sulphides.

4) *Reducing gases of deep-seated origin.* Emissions of reducing gases that have migrated through the lithosphere have been suggested by many authors, see e.g. Gold & Soter (1980), Malmqvist & Kristiansson (1981, 1984, 1985), Mac Donald (1983), Kozlovsky (1984) and Oliver (1986). The gases may be biogenic (due to buried organic material) or abiogenic (mantle derived or of other deep-seated origin).

5) *Cathodes in natural galvanic cells.* In connection with differences in electrical conductance in the bedrock (e.g. at occurrences of graphite horizons or sulphide bodies), natural potential differences (Self Potentials, SP) may be recorded at the surface or in drill holes. SP is a manifestation of a flow of natural electric currents in the lithosphere. The potential sources are thought to be galvanic cells caused by good conducting bodies (electrodes) that penetrate redox potential gradi-

ents in a less conductive country-rock (electrolyte). Such cells have reducing properties at their cathodic upper end (Bølviken 1979).

Our work has shown that there are no universal associations between oxidate sediment provinces and features such as bogs, sulphide mineralisations and Carboniferous shales. Therefore, life processes or one or both of the remaining two more obscure reducing agents would also play a role in the reduction of  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ . Gas emanations are probably more common than supposed earlier (Malmqvist & Kristiansson 1981, 1984, 1985). Natural galvanic cells may also provide an explanation why oxidate sediments more often are associated with magnetic than with non-magnetic granites. Magnetite contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and is a good electric conductor indicating that magnetic structures in a granite may form  $\text{Fe}^{2+}$  producing cathodes.

## Future work

Further research on oxidate sediments - in particular the role of different reducing agents in their formation - should be carried out for several reasons:

- Areas with common occurrences of oxidate sediments may be manifestations of 1) gas emanations over oil and mineral deposits or 2) electrically conducting structures beneath the surface. Both point to the possibility of using surveys of oxidate sediments as a tool in exploration.
- Large reservoirs of oxidate sediments may have a buffering effect when exposed to acid rain, and precipitating oxidate sediments probably function as traps for heavy metal pollutants in surface waters. On the other hand, the heavy metals in oxidate sediments could be in a form that may be easily mobilised by excessive amounts of acid rain and thereby cause harmful effects.
- Deposits of oxidate sediments are probably associated with characteristic flora and fauna which are adapted to the specific geochemical conditions. Local and regional occurrences of oxidate sediments are, therefore, of interest in environmental health and geomedicine.

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